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CLAIMS

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(57) [Claim(s)]

[Claim 1] A fullerene thin film and the insulating layer prepared in contact with this fullerene thin film, It comes to have the 1st electrode prepared in contact with this insulating layer, and the 2nd electrode prepared in contact with the above-mentioned fullerene thin film. Said 1st electrode A lithium, sodium, magnesium, aluminum, A potassium, an indium, calcium, zinc, a scandium, titanium, It consists of manganese, a zirconium, a gallium, niobium, antimony, and one or more sorts of ingredients chosen from the group which consists of samarium. Said 2nd electrode Palladium, a tellurium, a rhenium, iridium, copper, Silver, gold, platinum, a ruthenium, germanium, the tin oxide, indium oxide, Tunnel diode characterized by consisting of one or more sorts of ingredients chosen from the group which consists of the tin oxide which carried out the heavy dope by indium oxide, a zinc oxide, graphite, glassy carbon, a silver paste, and carbon paste.

[Claim 2] Tunnel diode according to claim 1 characterized by a fullerene thin film being a thin film which consists of carbon clusters.

[Claim 3] Tunnel diode according to claim 2 characterized by a fullerene thin film being a thin film which consists of a carbon cluster C60 and/or a carbon cluster C70.

[Claim 4] Tunnel diode according to claim 1 to 3 with which a fullerene thin film is characterized by being the vacuum deposition film, the cast film, or the polymer distribution film.

[Claim 5] Tunnel diode according to claim 1 to 4 characterized by for the 1st electrode being aluminum and being the electrode which consists of one or more sorts of ingredients chosen from the group which the 2nd electrode becomes from platinum, gold, silver, copper, the tin oxide, and indium oxide.

[Claim 6] Tunnel diode according to claim 5 with which an insulating layer is characterized by being an aluminum oxide layer and/or a silicon oxide layer.

[Claim 7] Tunnel diode according to claim 5 characterized by an insulating layer being a layer which heat-treated the aluminum layer and was generated.

[Claim 8] Tunnel diode according to claim 1 to 7 with which an insulating layer is characterized by being a layer with a thickness of 30-150A.

[Claim 9] Tunnel diode according to claim 1 to 8 with which a fullerene thin film is characterized by being sandwiched with the 1st electrode and 2nd electrode.

[Claim 10] Tunnel diode according to claim 1 to 9 with which tunnel diode is characterized by being a rectifying device.

[Claim 11] Tunnel diode according to claim 1 to 9 with which tunnel diode is characterized by being a photosensor.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] Especially this invention relates to the tunnel diode which has the outstanding rectifying action and the outstanding photoconductivity with respect to an organic-semiconductor component.
[0002]
[Description of the Prior Art] In the field of a semiconductor device, inorganic substances, such as sulfuration cadmium NIUMU, a zinc oxide, crystal silicon, an amorphous silicon, and gallium arsenide, have been used conventionally. These are used for a transistor, a rectifying device, IC and LSI, the photosensor, the solar battery, etc. Generally the tunnel diode which does the tunnel effect so in these semiconductor devices consists of a PN junction or (Metal M)-(insulating-layer I)-semi-conductor (S) junction (MIS junction), in the case of a PN junction, P and N are doped to high concentration, and in MIS junction, the thickness of an insulating layer (I) is regulated in the specific range, and it is constituted. And in the case where ** insulating layer is comparatively thick, it sets to the current-voltage characteristic. A configuration shows the current maximum at the time of the forward direction or reverse voltage impression, and the description which a current value decreases by negative resistance, and begins to increase is acquired after that. In the case where ** insulating layer is comparatively thin in the current-voltage characteristic, the description from which a current value becomes fixed in the fixed electrical-potential-difference range is acquired ("Physics of Semiconductor Devices" --) 2nd (s) Edition, S.M.Sze, John Wiley & Sons, NY, 513 pages (1981). Such tunnel diode is used for a high-speed switching element, a multivibrator, a high-speed logical circuit, or a low noise microwave amplifier with the property. However, in order to produce these semiconductor devices using the above inorganic substances, advanced vacuum devices, an advanced film production technique, advanced purity regulation, etc. were required, and the production was what cannot be released easily.
[0003] On the other hand, the versatility of the organic substance, semi-conductor nature, etc. began to attract attention, and great research has been made about the semi-conductor nature of organic compounds, such as polyacethylene, polypyrrole, and a phthalocyanine, and conductivity ("new and a conductive polymer", **** Hiroyuki editorial supervision, CMC, (1987)). and as a semiconductor device which comes to pinch a conductive polymer or a semi-conductor nature organic compound with a metal Polyacethylene, the poly diacetylene, polypyrrole, alpha-sesquithienyl, MS component which comes to pinch semi-conductor thin films (S), such as a phthalocyanine, with a metal electrode (M), Or the MIS component which comes to pinch the thin film (I) of an insulator among them, many components are proposed ("Physics of Semiconductor Devices" --) 2nd(s) Edition, S.M.Sze, John Wiley & Sons, NY (1981), D.Fichou, F.Garnieret al., CHEMTRONICS, 1988, 176 pages.
[0004] These organic compounds show the semi-conductor nature of P type or N type, and when this is pinched with the small electrode of a work function, and the large electrode of a work function as compared with the Fermi level of the organic compound, they show a rectifying action. For example, when this is pinched with an aluminum electrode and an indium tin oxide (or

gold) electrode in the case of alpha-sesquithienyl (D. Fichou, F.Garnier et al., CHEMTRONICS, 1988, 176 pages), **1V show the rectifying action of 100 times or more. Furthermore, the example (Pt| polypyrrole | poly thiophene |In, M.Aizawa, H.Shirakawa, Synth.Met., No. 18, and 711 pages (1987)) which built the rectifying device by junction of a different-species conductive polymer and FET The built example (H. Koezuka, etal., Synth.Met., No. 18, and 699 pages (1987)) is also known. Moreover, since a phthalocyanine etc. shows a photoconductivity, the application to a solar battery etc. is considered and the solar battery which comes to pinch this with aluminum and ITO glass (electrically conductive glass by the tin-oxide thin film which carried out the heavy dope by indium oxide) is examined. However, the present condition is that a report of the tunnel diode using an organic compound is not found.

[0005]

[Problem(s) to be Solved by the Invention] the above-mentioned organic compound -- general -- the instability (for example, the instability over air, humidity, etc. of polyacethylene --) of **S layer, i.e., a conductive polymer layer, or an organic-semiconductor layer the fall (for example, alpha-sesquithienyl --) of repeatability by mixing of ** impurity, such as instability after doping A phthalocyanine etc. does not have the solvent which dissolves only concentrated-sulfuric-acid extent, and improvement in purity is very difficult for it. ** Indeterminacy at the time of component formation (mixing of the catalyst by the vapor phase polymerization, electrolytic polymerization, etc., an electrolyte, etc.) Mixing of the impurity by the pyrolysis at the time of vacuum deposition, such as alpha-sesquithienyl and a phthalocyanine, etc., ** The corrosion of the electrode after component formation (corrosion of the electrode by the dopant, promotion of oxidation of an aluminum electrode which is looked at by the phthalocyanine, etc.), ** It does not have problems, such as mechanical brittleness (if vacuum deposition film, such as alpha-sesquithienyl and a phthalocyanine, is rubbed, it will separate) of a thin film, and neither has resulted in utilization. Furthermore in a solar battery, it has not resulted [from the lowness of conversion efficiency] in the degradation with the passage of time and utilization. It is electrophotography photo conductor extent using the polymer battery which used the poly aniline, the capacitor using TCNQ, a phthalocyanine, etc. which was slightly put in practical use with the organic substance, and the present condition is that an outstanding result cannot be found.

[0006]

[Means for Solving the Problem] By preparing two or more electrodes using a fullerene thin film so that this may be touched as a result of inquiring wholeheartedly that this invention persons should improve these in view of the various faults like the above of organic semiconductors including the conventional conductive polymer It finds out that a tunnel diode property is acquired by preparing an insulating layer between an electrode and a fullerene layer using that a semiconductor device is easily obtained with sufficient repeatability, and a specific electrode, and came to complete this invention.

[0007] In order to solve said technical problem, namely, the tunnel diode of this invention A fullerene thin film and the insulating layer prepared in contact with this fullerene thin film, It comes to have the 1st electrode prepared in contact with this insulating layer, and the 2nd electrode prepared in contact with the above-mentioned fullerene thin film. Said 1st electrode A lithium, sodium, magnesium, aluminum, A potassium, an indium, calcium, zinc, a scandium, titanium, It consists of manganese, a zirconium, a gallium, niobium, antimony, and one or more sorts of ingredients chosen from the group which consists of samarium. Said 2nd electrode Palladium, a tellurium, a rhenium, iridium, copper, Silver, gold, platinum, a ruthenium, germanium, the tin oxide, indium oxide, It is characterized by consisting of one or more sorts of ingredients chosen from the group which consists of the tin oxide which carried out the heavy dope by indium oxide, a zinc oxide, graphite, glassy carbon, a silver paste, and carbon paste.

[0008] Hereafter, this invention is explained in detail. This invention offers the MIS tunnel diode which has a fullerene thin film (S), the insulating layer (I) which touches this, and the 1st electrode (M) which touches an insulating layer and the 2nd electrode which touches a fullerene thin film. Drawing 1 is what showed one example of the tunnel diode of this invention, and it is the sectional view where (a) meets a top view and (b) meets the A-A line in (a). The 1st three

electrode 2a, 2a, and 2a with which the tunnel diode shown in drawing 1 was formed in the shape of a strip of paper on the insulating substrate 1 is formed in parallel. An insulating layer 3 is formed in the top face of these 1st electrodes 2a, 2a, and 2a, and the fullerene thin film 4 is formed in the top face of an insulating layer 3 and an insulating substrate 1. It is prepared so that the 1st electrode 2a, 2a, and 2a of the above, and 2nd three electrode 2b, 2b and 2b which were furthermore formed in the shape of a strip of paper on this fullerene thin film 4 may cross at right angles in parallel. An insulating layer 3 may be formed here the whole surface not only a 1st electrode 2a top but on the 1st electrode 2a and a substrate 1. Furthermore, protective coats, such as insulating polymer film or an insulating metallic oxide, can also be formed if needed on 2nd electrode 2b, 2b, 2b, and the fullerene thin film 4. Moreover, the number of the 1st electrode and the 2nd electrodes can be set or more to one at arbitration, respectively.
[0009] The fullerene thin film 4 used by this invention is a thin film formed using fullerene. here, it becomes fullerene from sp2 carbon -- it is the generic name of the carbon cluster of the shape of spherical or a Rugby ball, and, generally C60, C70, C76, C78, C82, C84, C90, and C96 grade are known. These contain carbon in arc discharge or the middle class of soot which carry out resistance heating, and it was made to evaporate, it quenched with inert gas, such as helium, and was generated, and C60 (for example, Nature(s), such as Kraetschmer, No. 347, 354 etc. pages (1990), etc.) contains them. [most] And the mixture of the above-mentioned carbon cluster is obtained from this soot by extracting, for example with solvents, such as a hexane, benzene, toluene, a mesitylene, and a carbon disulfide. for refining this mixture furthermore and isolating respectively -- usually -- purification of an organic compound -- business -- **** -- a chromatography -- technique (for example, Nature(s), such as Kraetschmer, No. 347, 354 etc. pages (1990), etc.) can be used. In this invention, the mixed fullerene by which composition and isolation perform extract and insoluble impurity removal, and are acquired from the soot containing C60 or C70, or these is used preferably. [easy]
[0010] The fullerene thin film 4 can be formed by various kinds of film production approaches, and can be used, for example, the vacuum deposition film, the cast film, the polymer distribution film, etc. can be used. According to the technique of general vacuum deposition, fullerene is heated under the vacuum of 5x10 to 5 or less torrs using a metallicity boat or an alumina nature boat (the volume thin film handbooks and for 131st committee of the Japan Society for the Promotion of Science thin film, Ohm-Sha (1984), etc.), and the vacuum deposition film can form a thin film by putting a substrate on the upper part or lower part. Under the present circumstances, the need may be accepted, and a substrate may be heated or cooled. When a thin film is amorphous when a substrate is cooled, and it heats more than a room temperature or it, it is obtained as a crystallized state. The vacuum deposition film of these fullerene is very firmly [stably] firm in air. For example, the conventional phthalocyanine, alpha-sesquithienyl, etc. will separate, if it rubs, and to being inferior to a mechanical strength so that it can exfoliate easily with a Scotch tape (trademark) etc., even if it rubs the vacuum evaporationo film of fullerene, it does not separate easily, but it is firm film which cannot exfoliate and is excellent in a Scotch tape (trademark) at a mechanical strength.
[0011] The cast film is the means which uses the property which for example, fullerene dissolves in aromatic hydrocarbon, such as benzene, toluene, and a mesitylene, a carbon disulfide, n-hexane, etc., and can create a thin film simple. Namely, make it dissolve in the above-mentioned solvent etc., and it is dropped on a substrate, or a substrate is fixed on a spinner. After the above-mentioned solution is dropped, make it rotate at a suitable rotational frequency, and thin-film-ize a spinner. Or with the means of thin-film-izing the solution dropped on the substrate using a bar coating machine or a doctor blade, it can thin-film-ize and, subsequently a film can be produced air drying, heat, or by drying with means, such as carrying out a vacuum drying.
[0012] The polymer distribution film can be produced with the same means as the above-mentioned cast film, after adding fullerene in the solution of a polymer and making it dissolve or distribute. As the distributed approach, the pigment-content powder technique, such as a paint shaker, a spec. SUMIKI sir mill, a sand mill, a ball mill, ATORATA, and a kneader, can be used. As a polymer which can be used here, although there is especially no limit, when an example is given, there are copolymers, such as fluorination polymers, such as vinyl system polymers, such

as saturated polyester, unsaturated polyester, a polycarbonate, a polyvinyl chloride, Pori acetic-acid vinyl, a poly vinyl carbazole, and styrene, fluoride poly vinylidene, and fluoride polyvinyl, and a styrene-maleic acid, etc. Moreover, for example, liquid crystal macromolecules, such as a polyacrylate system liquid crystal macromolecule and a polysiloxane system liquid crystal macromolecule, can also be used.
[0013] About the thickness of the fullerene thin film 4 which constitutes tunnel diode, since it will be easy to short-circuit each other electrode if too thin, a thing with a certain amount of thickness is desirable. Therefore, the range of 100A - 100 micrometers is suitable for the thickness of the fullerene thin film 4, and the range of it is 200A - 10 micrometers especially preferably.
[0014] In order to pull out the semi-conductor nature which was excellent in fullerene, it is required to prepare 1st electrode 2a which touches the fullerene thin film 4 through an insulating layer 3 at least, and 2nd electrode 2b which touches the fullerene thin film 4. As these electrodes, a metal electrode, a metallic-oxide electrode, a carbon electrode, etc. can be used, for example. As the 1st electrode 2a, if it illustrates, metals, such as a lithium, sodium, magnesium, aluminum, a potassium, an indium, calcium, zinc, a scandium, titanium, manganese, a zirconium, a gallium, niobium, antimony, and samarium, can be used, and especially aluminum is used preferably.
[0015] As 2nd electrode 2b, for example Moreover, palladium, a tellurium, a rhenium, Iridium, copper, silver, gold, platinum, a ruthenium, germanium, the tin oxide (for example, NESA glass), Although a metal or metallic oxides, such as the tin oxide (for example, ITO glass) which carried out the heavy dope by indium oxide and indium oxide, a zinc oxide, graphite, glassy carbon, a silver paste, and carbon paste, etc. are used Especially, platinum, gold, silver, copper, the tin oxide (for example, NESA glass, NESA coat polymer film), and indium oxide (for example, ITO glass, ITO coat polymer film) are desirable.
[0016] A metal plate, a carbon plate, a thin film, the conductive paint film, etc. can be used for these electrodes with any gestalt. When using it with the gestalt of a thin film, it can be used with the means of a metallic foil, the vacuum evaporationo film, the sputtering film, an electrodeposited film, the spray pyrolysis film, etc., thin-film-izing. Moreover, a conductive paint (for example, silver, a carbon content coating) can be applied, and an electrode can also be formed. Here, when preparing an electrode by film production or spreading, it is desirable to use a substrate 1. As this substrate 1, there is especially no limit and its insulating thing is desirable. As the example, a glass plate, a quartz plate, an insulating polymer plate, etc. are mentioned. Moreover, especially when using tabular electrodes, such as a metal plate and a carbon plate, as an electrode, it is not necessary to use a substrate 1.
[0017] In the tunnel diode of this invention, in order to acquire the tunnel effect, it is an indispensable condition to have the thin insulating layer 3 between 1st electrode 2a with a small work function and the fullerene thin film 4. As this insulating layer 3, a metallic oxide, an organic compound, a polymer insulating layer, etc. can be used. As a metal oxide layer, aluminum oxide, oxidization silicon, indium oxide, the tin oxide, titanium oxide, etc. are mentioned. As an organic compound or a polymer insulating layer, that what is necessary is just a usual insulating organic compound or a usual polymer, if it illustrates, a fatty acid, long-chain alcohol, polyethylene, a polyvinyl chloride, a polyacrylonitrile, an epoxy resin, a polyamide, etc. will be mentioned. In addition, this invention is not limited to the compound of instantiation here.
[0018] These insulating layers 3 can be easily formed by technique, such as vacuum evaporationo, sputtering, casting, and LB film. Moreover, the formation of an aluminum oxide and oxidation silicon is desirable especially from an easy thing as an insulating layer 3. In the case of an aluminum oxide insulating layer, this can be easily formed by heat-treating the aluminum layer obtained by vacuum evaporationo in oxygen content gases, such as air. An oxidation silicon insulating layer can form this easily by carrying out sputtering of the silicon under an oxygen ambient atmosphere, or heat-treating the vacuum evaporationo film of silicon in oxygen content gases, such as air. In these insulation layer forming processes, although especially heat treatment temperature is not restricted, the temperature of 50-1000 degrees C is desirable also from the point of workability. Especially when oxidizing an aluminum layer, the temperature of

50-200 degrees C is suitable, and when oxidizing a silicon layer, the temperature of 200-800 degrees C is suitable. Moreover, in the configuration of tunnel diode, especially the thickness of an insulating layer 3 is especially important, and its thickness of 30-150A is desirable 10-200A.
[0019] The tunnel diode of this invention is the following, and can be made and produced. A substrate 1 is prepared first. Next, 1st electrode 2a is formed with means, such as vacuum evaporationo or sputtering, on the substrate 1. And in being the metal electrode with which this 1st electrode 2a tends to oxidize, it heat-treats in oxygen content gases, such as air, and forms the oxide insulating layer 3. Furthermore, the fullerene thin film 4 is formed with the means of vacuum evaporationo, casting, or the polymer distribution film on the insulating layer 3. Subsequently, tunnel diode is producible by forming 2nd electrode 2b with means, such as vacuum evaporationo and sputtering, on the fullerene thin film 4. Or after forming the 2nd metal electrode first on the insulating substrate 1, sequential film production of the fullerene thin film 4, an insulating layer 3, and the 1st electrode 2a can be carried out, and tunnel diode can also be produced.
[0020] After the maximal value of a current is shown in current-voltage characteristic measurement in the dark when the sweep of the electrical potential difference is carried out to hard flow from 0V if it is in the tunnel diode of this invention, in order to show negative resistance subsequently, the current value decreases, the increment in a current value is accepted after that, and the characteristic property as tunnel diode is acquired.
[0021] Moreover, the tunnel diode of this invention can show the outstanding rectifying action and a photoconduction property, and does not become unable to accept [but] the application as tunnel diode, i.e., a high-speed switching element, a multivibrator, a high-speed logical circuit, a low noise microwave amplifier, etc., but can be used also for a rectifying device, an optical switch, and a photosensor while it shows the outstanding tunnel diode property.
[0022] In addition, the tunnel diode of this invention is not limited to the configuration of the above-mentioned example, and various gestalten are possible for it and it may consist of a crystal, powder, etc. Moreover, various gestalten can be taken by the purpose of using tunnel diode, and based on these purposes, the configuration of an electrode and a component is changed suitably and it deals in it.
[0023] Here, thickness of an electrode can be made arbitrary when using it as tunnel diode and a rectifying device. On the other hand, when using it as a photosensor, the electrode of the side which carries out incidence of the light needs to be translucent. Although the range whose permeability of light is 98% - 0.1% is used when using an oxide electrode, the responsibility over light has the high one where the permeability of light is larger. In the case of a metal electrode, the responsibility over light has the high one where the permeability of light is larger, but if permeability is too large, an electrode will not conduct a current. Therefore, as for the permeability of light, 50% - 0.1% of range is used suitably.
[0024] What used the configuration of an electrode as the sandwiches electrode as shown in drawing 1 can be used suitable for the integrated rectifying devices (for example, switching element etc.), for example, can drive liquid crystal, ECD, etc. Or it can use suitably also as photosensors (for example, image sensors etc.). Electric field can be impressed to the 1st electrode 2a and 2nd electrode 2b which go direct mutually from an outdrive unit (not shown) in these cases, and it can use as a rectifying device or a photosensor.
[0025] Drawing 2 is what showed other examples of the tunnel diode of this invention which used the sandwiches electrode, and it is the sectional view where (a) meets a top view and (b) meets the A-A line in (a). 1st electrode 2a is prepared on an insulating substrate 1, an insulating layer 3 is formed on this 1st electrode 2a (or the 1st electrode 2a and the whole insulating-substrate 1 top surface), all over that upper part, the fullerene thin film 4 is formed and, as for this thing, 2nd electrode 2b formed in the shape of a strip of paper on the fullerene thin film 4 is prepared further. The number of these 2nd electrode 2bs is set as the number of one or more arbitration, and can carry out things. In addition, what kind of configurations, such as not only the shape of a strip of paper but a circle, an ellipse, etc., are sufficient as 2nd electrode 2b. 1st electrode 2a leaves one edge section 1a of substrate 1 top face, and is formed in band-like [thick]. Moreover, 2nd electrode 2b It intersects perpendicularly with the longitudinal direction of 1st

electrode 2a formed previously, it is prepared so that it may be crossed and located on edge section 1a of the above-mentioned insulating substrate 1 from on 1st [of a parenthesis] electrode 2a, and it can prevent un-arranging [which wiring from the 1st electrode and 2nd electrode short-circuits by this]. Moreover, protective coats, such as insulating polymer film or an insulating metallic oxide, can also be formed on 2nd electrode 2b and the fullerene thin film 4 if needed. Thus, the constituted tunnel diode can be used effective in an independent rectifying device, a transistor, a photosensor, etc.

[0026]

[Example] (Example 1) The tunnel diode which has the configuration shown in drawing 1 was produced. On slide glass 1, 1st electrode 2a of width of face of 3mm and a die-length 20mm configuration was formed with three pieces and vacuum deposition at intervals of 3mm. Aluminum was used for this electrode 2a, and it formed in the thickness of 200A under the vacuum of 5x10-5torr. Put this electrode 2a and the slide glass 1 in which three pieces were formed on 20cm on the alumina crucible of a vacuum deposition machine, and put the carbon cluster C60 into the crucible made from an alumina, and it was made to vapor-deposit, heating at 520-550 degrees C under the vacuum of 5x10-6torr (5A/(second)), and the vacuum deposition film 4 of C60 was formed in the thickness of 1000A. Subsequently, golden electrode 2b and three pieces were formed in the thickness of 200A, and the component was produced. It put in into the oven which heated this component at 100 degrees C, and heat-treated under the air ambient atmosphere for 20 minutes. According to measurement by the ellipsomter, at this time, the aluminum oxide layer 3 was formed between aluminum electrode 2a and C60 thin film 4 at the thickness of 60A.

[0027] Thus, the obtained component was held to in the dark, the function generator was used for 1st electrode (aluminum) 2a, and the triangular wave of **3.6V was impressed to it with the trace speed of 0.001Hz. At this time, the flowing current was measured using the electrometer. the current-voltage characteristic acquired by measurement -- a piece -- a logarithm -- (a) showed among drawing 3 as a Fig. Among drawing 3 , in (a), ** shows the forward current-voltage characteristic and ** shows the reverse current-voltage characteristic. In addition, although there was an actual measurement of the current at the time of minus electrical-potential-difference impression by minus in drawing 3 , the absolute value of a current showed here. The maximal value was first shown in the -0.5V neighborhood at the time of reverse voltage impression, the current value decreased by the negative resistance which is subsequently a tunnel diode property, and it was admitted that a current value increased from the -2V neighborhood so that clearly from drawing 3 . Moreover, the rectifying characteristic which whose rectification ratio of **2V is 151 and was excellent was also accepted. Furthermore, the repeatability in nine components which consist of lap parts of a rectangular electrode was also good. Moreover, although the Scotch tape (trademark) was stretched on the vacuum deposition film of C60 and subsequently being removed, C60 vacuum-deposition film has arrived at the substrate firmly, and did not separate. Furthermore, although EPOSHIKI resin performed the protection coat on the front face of this component, it was almost changeless to tunnel current and a rectifying characteristic. Therefore, the component obtained by this example has the engine performance which was excellent as tunnel diode and a rectifying device, and having excelled also in repeatability and a mechanical strength was admitted.

[0028] (Example 1 of a comparison) In the example 1, the component was similarly formed except not performing heat-treatment for forming an aluminum oxide layer. And this was saved under the vacuum after component formation. The current-voltage characteristic in the dark was measured like the example 1 immediately after component formation. The result was shown as (b) among drawing 3 . Among drawing 3 , in (b), ** shows the forward current-voltage characteristic and ** shows the reverse current-voltage characteristic. The component obtained here did not show the negative resistance and the rectifying action which are a tunnel diode property, but the rectification ratios of **1V were 1.2 and the value which was very inferior.

[0029] (Example 2) +2V were impressed to the aluminum electrode of the component produced like the example 1, and the homogeneous light of the wavelength of 400nm and optical on-the-strength 100 microwatt/cm 2 was irradiated. The big photocurrent of 1.3microA/cm2 was

observed at this time, and it was admitted that the obtained component was excellent also as a photosensor. Furthermore, the photocurrent has been observed even if it changed wavelength in 400-800nm. Moreover, the repeatability in nine components which consist of lap parts of a rectangular electrode was also good.

[0030] (Example 2 of a comparison) The component was produced like the example 1 of a comparison. The 400nm same homogeneous light as an example 2 was irradiated at the aluminum electrode of the component immediately after production. Although the photocurrent of 0.1microA/cm2 was observed at this time, this value was a very small value as compared with the value observed in the example 2.

[0031] (Example 3) The tunnel diode which has the configuration shown in drawing 2 was produced. Up 0.5mmx3cm of the 2cmx3cm glass substrate 1 was covered, and on this substrate 1, vacuum deposition of the aluminum was carried out to the thickness of a 200 ONGUSU toe ROM, and it was referred to as electrode 2a (permeability of the 400nm homogeneous light; 2.18%). It once took out with this condition into air, and put in into the 80-degree C thermostat, annealing was performed under the air ambient atmosphere for 30 minutes, and the aluminum oxide layer 3 was formed on electrode 1a. The thickness of the aluminum oxide layer 3 was 100A in measurement of an ellipsomter. Furthermore, on this oxide layer 3, vacuum deposition of C60 was carried out to 1000A thickness like the example 1, and the vacuum deposition film 4 of C60 was formed. Subsequently, on it, vacuum deposition of 0.5cmx1.5cm copper-electrode 2b and the three pieces was carried out, and the component was formed. When the triangular wave which is -1V to +1V was impressed to this component from the function generator (scanning speed; 0.002Hz), the current-voltage characteristic showed the same tunnel diode property as (a) among drawing 3 . Moreover, repeatability was good about three electrodes.

[0032] (Example 3 of a comparison) 2000A of alpha-sesquithienyls was vapor-deposited like the example 3 on the top face of the glass plate 1 in which aluminum electrode 2a and the aluminum oxide layer 3 were formed (20A/(second)). If it is very hard to vapor-deposit alpha-sesquithienyl and it is vapor-deposited slowly, it will serve as film which decomposed and contained many impurities. Although decomposition will decrease if it vapor-deposits quickly (20A/(second) or more), an impurity is contained too. Subsequently, 0.5cmx1.5cm copper-electrode 2b and three pieces were formed by vacuum evaporationo. The triangular wave of -2 to +2V was impressed to the obtained component from the function generator (0.002Hz). This component showed a rectifying action, or did not show it, and its repeatability was very bad. Furthermore, negative resistance characteristic as tunnel diode was not observed at the time of the forward direction and reverse voltage impression.

[0033] (Example 4) The tunnel diode which has the configuration shown in drawing 2 was produced. On slide glass 1, indium electrode 2a was formed like the example 3. Then, the silicon oxide thin film 3 was formed by sputtering the whole surface on slide glass 1 and electrode 2a. Besides, it extracted from soot, vacuum deposition of this was carried out to the thickness of 1000A using fullerene mixing (containing C70 for C60 19% 80% in liquid chromatography analysis, remaining 1% was a 70 or more C high order fullerene compound) which removed insoluble matter with the chromatography, and the fullerene thin film 4 was formed. Subsequently, on it, vacuum deposition of 0.5cmx1.5cm silver electrode 2b and the three pieces was carried out, and the component was formed. When the current-voltage characteristic of the obtained component was measured like the example 3, when a minus electrical potential difference was impressed to an indium electrode, negative resistance was accepted, and it has checked that a tunnel diode property was shown.

[0034] (Example 5) In the configuration shown in drawing 2 , the tunnel diode which has the configuration which made reverse 1st electrode 2a and sequence of 2nd electrode 2b was produced. Width of face of 0.5cm and die length of 3cm were etched with the hydrochloric acid on 3cm 2cmx ITO glass 1, the conductive film was removed (part equivalent to 1in drawing 2 a), and the conductive remaining film was made into indium oxide (ITO) electrode 2b. On this electrode 2b, the dispersion liquid (60; 20mg of C, vinyl acetate;20mg, ethyl acetate; dispersion liquid which put the glass bead into 200mg and were distributed with the paint shaker for 1 hour) which made vinyl acetate / ethyl-acetate solution distribute C60 were thin-film-ized using bar

coating-machine #4, and the polymer distribution film 4 of C60 was produced. The vacuum drying of this film 4 was carried out at 100 degrees C for 1 hour. Thickness was 0.2 micrometers. Subsequently, by carrying out sputtering of the silicon in an oxygen ambient atmosphere on this film 4, the silicon oxide layer was made to form in the thickness of 80A, on it, vacuum deposition of the three aluminum (width-of-face [of 0.5cm], die length of 1.5cm) electrode 2a was carried out, and the component was constituted. The triangular wave of -2V to +2V was impressed at a scanning speed of 0.001Hz from the function generator between this indium oxide electrode 2b and aluminum electrode 2a. The current-voltage characteristic at this time showed negative resistance like (a) among drawing 3 at the time of reverse voltage impression, and also showed the rectifying action. Moreover, the repeatability in 3 sets of formed electrodes was good. Moreover, even if it carried out the protection coat of the whole with the epoxy resin, the current-voltage characteristic hardly changed. Therefore, the component obtained by this example has the engine performance which was excellent as tunnel diode and a rectifying device, and having excelled also in repeatability was admitted.
[0035] (Example 6) Tunnel diode was produced in the above-mentioned example 5, using the cast film as a fullerene thin film 4. Like the example 5, on indium oxide electrode 2b which etched indium tin glass 1 and was obtained, the liquid made to dissolve the carbon cluster C60 in toluene was dropped, and the cast film 4 of C60 was produced using the spinner. The vacuum drying was carried out at 100 more degrees C for 1 hour. Others formed the component similarly. When the electrical potential difference of 1V was impressed to this component and the homogeneous light of 400nm and 1 mW/cm2 was irradiated, the photocurrent of 1.5A was observed. Moreover, this component showed the good rectifying action and the tunnel diode property like the thing of an example 5.
[0036] (Example of reference) Commercial crude soot was refined and C60 and C70 were obtained. First, 4g (vacuum metallurgy incorporated company make) of crude soot containing fullerene was put into the extraction thimble, and it extracted by n-hexane;200ml for 24 hours using the Soxhlet extractor. Subsequently, the solvent was changed into mesitylene;200ml and the extract was performed for further 24 hours. When the first n-hexane solution was analyzed by liquid chromatography (silica gel - n-hexane), the ratio of C60:C70 is 9:1 and did not contain most of 76 or more C fullerene. The ratio of C60:C70 is about 6:4, and the mesitylene extract was carrying out variety content of the 76 or more C fullerene. n-hexane extract was condensed by the evaporator and 0.26g fullerene mixture was obtained. Using the ODS column, the mixed solvent of a 2-propanol / toluene;6/4 was used as the developing solution, and 0.21g and 0.02g of high grades C70 were obtained for the high grade C60 using inside low voltage preparative chromatograph. The mesitylene extract was condensed by the evaporator and mixed fullerene 0.13g was obtained. It isolated preparatively by the chromatograph similarly and mixture;0.01g of 60; 0.07g of high grades C, 70; 0.04g of high grades C, and other fullerene was obtained. Mixture contained C76, C78, C84, and fullerene with still larger molecular weight from GC-MS analysis.
[0037]
[Effect of the Invention] As explained above, the tunnel diode of this invention A fullerene thin film and the insulating layer prepared in contact with this fullerene thin film, It comes to have the 1st electrode prepared in contact with this insulating layer, and the 2nd electrode prepared in contact with the above-mentioned fullerene thin film. Said 1st electrode A lithium, sodium, magnesium, aluminum, A potassium, an indium, calcium, zinc, a scandium, titanium, It consists of manganese, a zirconium, a gallium, niobium, antimony, and one or more sorts of ingredients chosen from the group which consists of samarium. Said 2nd electrode Palladium, a tellurium, a rhenium, iridium, copper, Silver, gold, platinum, a ruthenium, germanium, the tin oxide, indium oxide, It is characterized by consisting of one or more sorts of ingredients chosen from the group which consists of the tin oxide which carried out the heavy dope by indium oxide, a zinc oxide, graphite, glassy carbon, a silver paste, and carbon paste. The tunnel diode of this invention can show the outstanding rectifying action and the outstanding photoconductivity, and can constitute various kinds of semiconductor devices, using this suitably while it shows the outstanding tunnel diode property. And the fullerene used by this invention is easy to compound, and in order to dissolve in a solvent, it is easy to refine, and it can obtain a high grade article

easily. Moreover, thermal resistance is also high, and since the decomposition at the time of vacuum evaporationo does not take place, either, component-ization can be performed easily. Therefore, tunnel diode with sufficient repeatability is obtained. Moreover, these fullerene can be used also in the form of the cast film which does not need a vacuum, and the polymer distribution film. Therefore, good stability and repeatability are acquired by using the fullerene thin film which the tunnel diode of this invention produces fullerene and is obtained. Furthermore, since the engine performance does not change even if it gives the protection coat which used resin etc., the tunnel diode of this invention can be used for an extensive application. Especially, it is broadly applicable to driver elements, such as a rectifying device, liquid crystal using a rectifying action, and an ECD component, a photosensor, or the image sensors adapting a photosensor function.

[Translation done.]

TECHNICAL FIELD

[Industrial Application] Especially this invention relates to the tunnel diode which has the outstanding rectifying action and the outstanding photoconductivity with respect to an organic-semiconductor component.

[Translation done.]

PRIOR ART

[Description of the Prior Art] In the field of a semiconductor device, inorganic substances, such as sulfuration cadmium NIUMU, a zinc oxide, crystal silicon, an amorphous silicon, and gallium arsenide, have been used conventionally. These are used for a transistor, a rectifying device, IC and LSI, the photosensor, the solar battery, etc. Generally the tunnel diode which does the tunnel effect so in these semiconductor devices consists of a PN junction or (Metal M)-(insulating-layer I)-semi-conductor (S) junction (MIS junction), in the case of a PN junction, P and N are doped to high concentration, and in MIS junction, the thickness of an insulating layer (I) is regulated in the specific range, and it is constituted. And in the case where ** insulating layer is comparatively thick, it sets to the current-voltage characteristic. A configuration shows the current maximum at the time of the forward direction or reverse voltage impression, and the description which a current value decreases by negative resistance, and begins to increase is acquired after that. In the case where ** insulating layer is comparatively thin in the current-voltage characteristic, the description from which a current value becomes fixed in the fixed electrical-potential-difference range is acquired ("Physics of Semiconductor Devices" --) 2nd (s) Edition, S.M.Sze, John Wiley & Sons, NY, 513 pages (1981). Such tunnel diode is used for a high-speed switching element, a multivibrator, a high-speed logical circuit, or a low noise microwave amplifier with the property. However, in order to produce these semiconductor devices using the above inorganic substances, advanced vacuum devices, an advanced film production technique, advanced purity regulation, etc. were required, and the production was what cannot be released easily.
[0003] On the other hand, the versatility of the organic substance, semi-conductor nature, etc. began to attract attention, and great research has been made about the semi-conductor nature of organic compounds, such as polyacethylene, polypyrrole, and a phthalocyanine, and conductivity ("new and a conductive polymer", **** Hiroyuki editorial supervision, CMC, (1987)). and as a semiconductor device which comes to pinch a conductive polymer or a semi-conductor nature organic compound with a metal Polyacethylene, the poly diacetylene, polypyrrole, alpha-sesquithienyl, MS component which comes to pinch semi-conductor thin films (S), such as a phthalocyanine, with a metal electrode (M), Or the MIS component which comes to pinch the thin film (I) of an insulator among them, many components are proposed ("Physics of Semiconductor Devices" --) 2nd(s) Edition, S.M.Sze, John Wiley & Sons, NY (1981), D.Fichou, F.Garnieret al., CHEMTRONICS, 1988, 176 pages.
[0004] These organic compounds show the semi-conductor nature of P type or N type, and when this is pinched with the small electrode of a work function, and the large electrode of a work function as compared with the Fermi level of the organic compound, they show a rectifying action. For example, when this is pinched with an aluminum electrode and an indium tin oxide (or gold) electrode in the case of alpha-sesquithienyl (D. Fichou, F.Garnier et al., CHEMTRONICS, 1988, 176 pages), **1V show the rectifying action of 100 times or more. Furthermore, the example (Pt| polypyrrole | poly thiophene |In, M.Aizawa, H.Shirakawa, Synth.Met., No. 18, and 711 pages (1987)) which built the rectifying device by junction of a different-species conductive polymer and FET The built example (H. Koezuka, etal., Synth.Met., No. 18, and 699 pages (1987)) is also known. Moreover, since a phthalocyanine etc. shows a photoconductivity, the application

to a solar battery etc. is considered and the solar battery which comes to pinch this with aluminum and ITO glass (electrically conductive glass by the tin-oxide thin film which carried out the heavy dope by indium oxide) is examined. However, the present condition is that a report of the tunnel diode using an organic compound is not found.

[Translation done.]

EFFECT OF THE INVENTION

[Effect of the Invention] As explained above, the tunnel diode of this invention A fullerene thin film and the insulating layer prepared in contact with this fullerene thin film, It comes to have the 1st electrode prepared in contact with this insulating layer, and the 2nd electrode prepared in contact with the above-mentioned fullerene thin film. Said 1st electrode A lithium, sodium, magnesium, aluminum, A potassium, an indium, calcium, zinc, a scandium, titanium, It consists of manganese, a zirconium, a gallium, niobium, antimony, and one or more sorts of ingredients chosen from the group which consists of samarium. Said 2nd electrode Palladium, a tellurium, a rhenium, iridium, copper, Silver, gold, platinum, a ruthenium, germanium, the tin oxide, indium oxide, It is characterized by consisting of one or more sorts of ingredients chosen from the group which consists of the tin oxide which carried out the heavy dope by indium oxide, a zinc oxide, graphite, glassy carbon, a silver paste, and carbon paste. The tunnel diode of this invention can show the outstanding rectifying action and the outstanding photoconductivity, and can constitute various kinds of semiconductor devices, using this suitably while it shows the outstanding tunnel diode property. And the fullerene used by this invention is easy to compound, and in order to dissolve in a solvent, it is easy to refine, and it can obtain a high grade article easily. Moreover, thermal resistance is also high, and since the decomposition at the time of vacuum evaporationo does not take place, either, component-ization can be performed easily. Therefore, tunnel diode with sufficient repeatability is obtained. Moreover, these fullerene can be used also in the form of the cast film which does not need a vacuum, and the polymer distribution film. Therefore, good stability and repeatability are acquired by using the fullerene thin film which the tunnel diode of this invention produces fullerene and is obtained. Furthermore, since the engine performance does not change even if it gives the protection coat which used resin etc., the tunnel diode of this invention can be used for an extensive application. Especially, it is broadly applicable to driver elements, such as a rectifying device, liquid crystal using a rectifying action, and an ECD component, a photosensor, or the image sensors adapting a photosensor function.

[Translation done.]

TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] the above-mentioned organic compound -- general -- the instability (for example, the instability over air, humidity, etc. of polyacethylene --) of **S layer, i.e., a conductive polymer layer, or an organic-semiconductor layer the fall (for example, alpha-sesquithienyl --) of repeatability by mixing of ** impurity, such as instability after doping A phthalocyanine etc. does not have the solvent which dissolves only concentrated-sulfuric-acid extent, and improvement in purity is very difficult for it. ** Indeterminacy at the time of component formation (mixing of the catalyst by the vapor phase polymerization, electrolytic polymerization, etc., an electrolyte, etc.) Mixing of the impurity by the pyrolysis at the time of vacuum deposition, such as alpha-sesquithienyl and a phthalocyanine, etc., ** The corrosion of the electrode after component formation (corrosion of the electrode by the dopant, promotion of oxidation of an aluminum electrode which is looked at by the phthalocyanine, etc.), ** It does not have problems, such as mechanical brittleness (if vacuum deposition film, such as alpha-sesquithienyl and a phthalocyanine, is rubbed, it will separate) of a thin film, and neither has resulted in utilization. Furthermore in a solar battery, it has not resulted [from the lowness of conversion efficiency] in the degradation with the passage of time and utilization. It is electrophotography photo conductor extent using the polymer battery which used the poly aniline, the capacitor using TCNQ, a phthalocyanine, etc. which was slightly put in practical use with the organic substance, and the present condition is that an outstanding result cannot be found.

[Translation done.]

* NOTICES *

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1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

MEANS

[Means for Solving the Problem] By preparing two or more electrodes using a fullerene thin film so that this may be touched as a result of inquiring wholeheartedly that this invention persons should improve these in view of the various faults like the above of organic semiconductors including the conventional conductive polymer It finds out that a tunnel diode property is acquired by preparing an insulating layer between an electrode and a fullerene layer using that a semiconductor device is easily obtained with sufficient repeatability, and a specific electrode, and came to complete this invention.
[0007] In order to solve said technical problem, namely, the tunnel diode of this invention A fullerene thin film and the insulating layer prepared in contact with this fullerene thin film, It comes to have the 1st electrode prepared in contact with this insulating layer, and the 2nd electrode prepared in contact with the above-mentioned fullerene thin film. Said 1st electrode A lithium, sodium, magnesium, aluminum, A potassium, an indium, calcium, zinc, a scandium, titanium, It consists of manganese, a zirconium, a gallium, niobium, antimony, and one or more sorts of ingredients chosen from the group which consists of samarium. Said 2nd electrode Palladium, a tellurium, a rhenium, iridium, copper, Silver, gold, platinum, a ruthenium, germanium, the tin oxide, indium oxide, It is characterized by consisting of one or more sorts of ingredients chosen from the group which consists of the tin oxide which carried out the heavy dope by indium oxide, a zinc oxide, graphite, glassy carbon, a silver paste, and carbon paste.
[0008] Hereafter, this invention is explained in detail. This invention offers the MIS tunnel diode which has a fullerene thin film (S), the insulating layer (I) which touches this, and the 1st electrode (M) which touches an insulating layer and the 2nd electrode which touches a fullerene thin film. Drawing 1 is what showed one example of the tunnel diode of this invention, and it is the sectional view where (a) meets a top view and (b) meets the A-A line in (a). The 1st three electrode 2a, 2a, and 2a with which the tunnel diode shown in drawing 1 was formed in the shape of a strip of paper on the insulating substrate 1 is formed in parallel. An insulating layer 3 is formed in the top face of these 1st electrodes 2a, 2a, and 2a, and the fullerene thin film 4 is formed in the top face of an insulating layer 3 and an insulating substrate 1. It is prepared so that the 1st electrode 2a, 2a, and 2a of the above, and 2nd three electrode 2b, 2b and 2b which were furthermore formed in the shape of a strip of paper on this fullerene thin film 4 may cross at right angles in parallel. An insulating layer 3 may be formed here the whole surface not only a 1st electrode 2a top but on the 1st electrode 2a and a substrate 1. Furthermore, protective coats, such as insulating polymer film or an insulating metallic oxide, can also be formed if needed on 2nd electrode 2b, 2b, 2b, and the fullerene thin film 4. Moreover, the number of the 1st electrode and the 2nd electrodes can be set or more to one at arbitration, respectively.
[0009] The fullerene thin film 4 used by this invention is a thin film formed using fullerene. here, it becomes fullerene from sp2 carbon — it is the generic name of the carbon cluster of the shape of spherical or a Rugby ball, and, generally C60, C70, C76, C78, C82, C84, C90, and C96 grade are known. These contain carbon in arc discharge or the middle class of soot which carry out resistance heating, and it was made to evaporate, it quenched with inert gas, such as helium, and was generated, and C60 (for example, Nature(s), such as Kraetschmer, No. 347, 354 etc. pages (1990), etc.) contains them. [most] And the mixture of the above-mentioned carbon

cluster is obtained from this soot by extracting, for example with solvents, such as a hexane, benzene, toluene, a mesitylene, and a carbon disulfide. for refining this mixture furthermore and isolating respectively -- usually -- purification of an organic compound -- business -- **** -- a chromatography -- technique (for example, Nature(s), such as Kraetschmer, No. 347, 354 etc. pages (1990), etc.) can be used. In this invention, the mixed fullerene by which composition and isolation perform extract and insoluble impurity removal, and are acquired from the soot containing C60 or C70, or these is used preferably. [easy]

[0010] The fullerene thin film 4 can be formed by various kinds of film production approaches, and can be used, for example, the vacuum deposition film, the cast film, the polymer distribution film, etc. can be used. According to the technique of general vacuum deposition, fullerene is heated under the vacuum of 5x10 to 5 or less torrs using a metallicity boat or an alumina nature boat (the volume thin film handbooks and for 131st committee of the Japan Society for the Promotion of Science thin film, Ohm-Sha (1984), etc.), and the vacuum deposition film can form a thin film by putting a substrate on the upper part or lower part. Under the present circumstances, the need may be accepted, and a substrate may be heated or cooled. When a thin film is amorphous when a substrate is cooled, and it heats more than a room temperature or it, it is obtained as a crystallized state. The vacuum deposition film of these fullerene is very firmly [stably] firm in air. For example, the conventional phthalocyanine, alpha-sesquithienyl, etc. will separate, if it rubs, and to being inferior to a mechanical strength so that it can exfoliate easily with a Scotch tape (trademark) etc., even if it rubs the vacuum evaporationo film of fullerene, it does not separate easily, but it is firm film which cannot exfoliate and is excellent in a Scotch tape (trademark) at a mechanical strength.

[0011] The cast film is the means which uses the property which for example, fullerene dissolves in aromatic hydrocarbon, such as benzene, toluene, and a mesitylene, a carbon disulfide, n-hexane, etc., and can create a thin film simple. Namely, make it dissolve in the above-mentioned solvent etc., and it is dropped on a substrate, or a substrate is fixed on a spinner. After the above-mentioned solution is dropped, make it rotate at a suitable rotational frequency, and thin-film-ize a spinner. Or with the means of thin-film-izing the solution dropped on the substrate using a bar coating machine or a doctor blade, it can thin-film-ize and, subsequently a film can be produced air drying, heat, or by drying with means, such as carrying out a vacuum drying.

[0012] The polymer distribution film can be produced with the same means as the above-mentioned cast film, after adding fullerene in the solution of a polymer and making it dissolve or distribute. As the distributed approach, the pigment-content powder technique, such as a paint shaker, a spec. SUMIKI sir mill, a sand mill, a ball mill, ATORATA, and a kneader, can be used. As a polymer which can be used here, although there is especially no limit, when an example is given, there are copolymers, such as fluorination polymers, such as vinyl system polymers, such as saturated polyester, unsaturated polyester, a polycarbonate, a polyvinyl chloride, Pori acetic-acid vinyl, a poly vinyl carbazole, and styrene, fluoride poly vinylidene, and fluoride polyvinyl, and a styrene-maleic acid, etc. Moreover, for example, liquid crystal macromolecules, such as a polyacrylate system liquid crystal macromolecule and a polysiloxane system liquid crystal macromolecule, can also be used.

[0013] About the thickness of the fullerene thin film 4 which constitutes tunnel diode, since it will be easy to short-circuit each other electrode if too thin, a thing with a certain amount of thickness is desirable. Therefore, the range of 100A - 100 micrometers is suitable for the thickness of the fullerene thin film 4, and the range of it is 200A - 10 micrometers especially preferably.

[0014] In order to pull out the semi-conductor nature which was excellent in fullerene, it is required to prepare 1st electrode 2a which touches the fullerene thin film 4 through an insulating layer 3 at least, and 2nd electrode 2b which touches the fullerene thin film 4. As these electrodes, a metal electrode, a metallic-oxide electrode, a carbon electrode, etc. can be used, for example. As the 1st electrode 2a, if it illustrates, metals, such as a lithium, sodium, magnesium, aluminum, a potassium, an indium, calcium, zinc, a scandium, titanium, manganese, a zirconium, a gallium, niobium, antimony, and samarium, can be used, and especially aluminum is used preferably.

[0015] As 2nd electrode 2b, for example Moreover, palladium, a tellurium, a rhenium, Iridium, copper, silver, gold, platinum, a ruthenium, germanium, the tin oxide (for example, NESA glass), Although a metal or metallic oxides, such as the tin oxide (for example, ITO glass) which carried out the heavy dope by indium oxide and indium oxide, a zinc oxide, graphite, glassy carbon, a silver paste, and carbon paste, etc. are used Especially, platinum, gold, silver, copper, the tin oxide (for example, NESA glass, NESA coat polymer film), and indium oxide (for example, ITO glass, ITO coat polymer film) are desirable.
[0016] A metal plate, a carbon plate, a thin film, the conductive paint film, etc. can be used for these electrodes with any gestalt. When using it with the gestalt of a thin film, it can be used with the means of a metallic foil, the vacuum evaporationo film, the sputtering film, an electrodeposited film, the spray pyrolysis film, etc., thin-film-izing. Moreover, a conductive paint (for example, silver, a carbon content coating) can be applied, and an electrode can also be formed. Here, when preparing an electrode by film production or spreading, it is desirable to use a substrate 1. As this substrate 1, there is especially no limit and its insulating thing is desirable. As the example, a glass plate, a quartz plate, an insulating polymer plate, etc. are mentioned. Moreover, especially when using tabular electrodes, such as a metal plate and a carbon plate, as an electrode, it is not necessary to use a substrate 1.
[0017] In the tunnel diode of this invention, in order to acquire the tunnel effect, it is an indispensable condition to have the thin insulating layer 3 between 1st electrode 2a with a small work function and the fullerene thin film 4. As this insulating layer 3, a metallic oxide, an organic compound, a polymer insulating layer, etc. can be used. As a metal oxide layer, aluminum oxide, oxidization silicon, indium oxide, the tin oxide, titanium oxide, etc. are mentioned. As an organic compound or a polymer insulating layer, that what is necessary is just a usual insulating organic compound or a usual polymer, if it illustrates, a fatty acid, long-chain alcohol, polyethylene, a polyvinyl chloride, a polyacrylonitrile, an epoxy resin, a polyamide, etc. will be mentioned. In addition, this invention is not limited to the compound of instantiation here.
[0018] These insulating layers 3 can be easily formed by technique, such as vacuum evaporationo, sputtering, casting, and LB film. Moreover, the formation of an aluminum oxide and oxidation silicon is desirable especially from an easy thing as an insulating layer 3. In the case of an aluminum oxide insulating layer, this can be easily formed by heat-treating the aluminum layer obtained by vacuum evaporationo in oxygen content gases, such as air. An oxidation silicon insulating layer can form this easily by carrying out sputtering of the silicon under an oxygen ambient atmosphere, or heat-treating the vacuum evaporationo film of silicon in oxygen content gases, such as air. In these insulation layer forming processes, although especially heat treatment temperature is not restricted, the temperature of 50-1000 degrees C is desirable also from the point of workability. Especially when oxidizing an aluminum layer, the temperature of 50-200 degrees C is suitable, and when oxidizing a silicon layer, the temperature of 200-800 degrees C is suitable. Moreover, in the configuration of tunnel diode, especially the thickness of an insulating layer 3 is especially important, and its thickness of 30-150A is desirable 10-200A.
[0019] The tunnel diode of this invention is the following, and can be made and produced. A substrate 1 is prepared first. Next, 1st electrode 2a is formed with means, such as vacuum evaporationo or sputtering, on the substrate 1. And in being the metal electrode with which this 1st electrode 2a tends to oxidize, it heat-treats in oxygen content gases, such as air, and forms the oxide insulating layer 3. Furthermore, the fullerene thin film 4 is formed with the means of vacuum evaporationo, casting, or the polymer distribution film on the insulating layer 3. Subsequently, tunnel diode is producible by forming 2nd electrode 2b with means, such as vacuum evaporationo and sputtering, on the fullerene thin film 4. Or after forming the 2nd metal electrode first on the insulating substrate 1, sequential film production of the fullerene thin film 4, an insulating layer 3, and the 1st electrode 2a can be carried out, and tunnel diode can also be produced.
[0020] After the maximal value of a current is shown in current-voltage characteristic measurement in the dark when the sweep of the electrical potential difference is carried out to hard flow from 0V if it is in the tunnel diode of this invention, in order to show negative resistance subsequently, the current value decreases, the increment in a current value is

accepted after that, and the characteristic property as tunnel diode is acquired.
[0021] Moreover, the tunnel diode of this invention can show the outstanding rectifying action and a photoconduction property, and does not become unable to accept [but] the application as tunnel diode, i.e., a high-speed switching element, a multivibrator, a high-speed logical circuit, a low noise microwave amplifier, etc., but can be used also for a rectifying device, an optical switch, and a photosensor while it shows the outstanding tunnel diode property.
[0022] In addition, the tunnel diode of this invention is not limited to the configuration of the above-mentioned example, and various gestalten are possible for it and it may consist of a crystal, powder, etc. Moreover, various gestalten can be taken by the purpose of using tunnel diode, and based on these purposes, the configuration of an electrode and a component is changed suitably and it deals in it.
[0023] Here, thickness of an electrode can be made arbitrary when using it as tunnel diode and a rectifying device. On the other hand, when using it as a photosensor, the electrode of the side which carries out incidence of the light needs to be translucent. Although the range whose permeability of light is 98% - 0.1% is used when using an oxide electrode, the responsibility over light has the high one where the permeability of light is larger. In the case of a metal electrode, the responsibility over light has the high one where the permeability of light is larger, but if permeability is too large, an electrode will not conduct a current. Therefore, as for the permeability of light, 50% - 0.1% of range is used suitably.
[0024] What used the configuration of an electrode as the sandwiches electrode as shown in drawing 1 can be used suitable for the integrated rectifying devices (for example, switching element etc.), for example, can drive liquid crystal, ECD, etc. Or it can use suitably also as photosensors (for example, image sensors etc.). Electric field can be impressed to the 1st electrode 2a and 2nd electrode 2b which go direct mutually from an outdrive unit (not shown) in these cases, and it can use as a rectifying device or a photosensor.
[0025] Drawing 2 is what showed other examples of the tunnel diode of this invention which used the sandwiches electrode, and it is the sectional view where (a) meets a top view and (b) meets the A-A line in (a). 1st electrode 2a is prepared on an insulating substrate 1, an insulating layer 3 is formed on this 1st electrode 2a (or the 1st electrode 2a and the whole insulating-substrate 1 top surface), all over that upper part, the fullerene thin film 4 is formed and, as for this thing, 2nd electrode 2b formed in the shape of a strip of paper on the fullerene thin film 4 is prepared further. The number of these 2nd electrode 2bs is set as the number of one or more arbitration, and can carry out things. In addition, what kind of configurations, such as not only the shape of a strip of paper but a circle, an ellipse, etc., are sufficient as 2nd electrode 2b. 1st electrode 2a leaves one edge section 1a of substrate 1 top face, and is formed in band-like [thick]. Moreover, 2nd electrode 2b It intersects perpendicularly with the longitudinal direction of 1st electrode 2a formed previously, it is prepared so that it may be crossed and located on edge section 1a of the above-mentioned insulating substrate 1 from on 1st [of a parenthesis] electrode 2a, and it can prevent un-arranging [which wiring from the 1st electrode and 2nd electrode short-circuits by this]. Moreover, protective coats, such as insulating polymer film or an insulating metallic oxide, can also be formed on 2nd electrode 2b and the fullerene thin film 4 if needed. Thus, the constituted tunnel diode can be used effective in an independent rectifying device, a transistor, a photosensor, etc.

[Translation done.]

EXAMPLE

[Example] (Example 1) The tunnel diode which has the configuration shown in drawing 1 was produced. On slide glass 1, 1st electrode 2a of width of face of 3mm and a die-length 20mm configuration was formed with three pieces and vacuum deposition at intervals of 3mm. Aluminum was used for this electrode 2a, and it formed in the thickness of 200A under the vacuum of 5x10-5torr. Put this electrode 2a and the slide glass 1 in which three pieces were formed on 20cm on the alumina crucible of a vacuum deposition machine, and put the carbon cluster C60 into the crucible made from an alumina, and it was made to vapor-deposit, heating at 520-550 degrees C under the vacuum of 5x10-6torr (5A/(second)), and the vacuum deposition film 4 of C60 was formed in the thickness of 1000A. Subsequently, golden electrode 2b and three pieces were formed in the thickness of 200A, and the component was produced. It put in into the oven which heated this component at 100 degrees C, and heat-treated under the air ambient atmosphere for 20 minutes. According to measurement by the ellipsomter, at this time, the aluminum oxide layer 3 was formed between aluminum electrode 2a and C60 thin film 4 at the thickness of 60A.
[0027] Thus, the obtained component was held to in the dark, the function generator was used for 1st electrode (aluminum) 2a, and the triangular wave of **3.6V was impressed to it with the trace speed of 0.001Hz. At this time, the flowing current was measured using the electrometer. the current-voltage characteristic acquired by measurement -- a piece -- a logarithm -- (a) showed among drawing 3 as a Fig. Among drawing 3 , in (a), ** shows the forward current-voltage characteristic and ** shows the reverse current-voltage characteristic. In addition, although there was an actual measurement of the current at the time of minus electrical-potential-difference impression by minus in drawing 3 , the absolute value of a current showed here. The maximal value was first shown in the -0.5V neighborhood at the time of reverse voltage impression, the current value decreased by the negative resistance which is subsequently a tunnel diode property, and it was admitted that a current value increased from the -2V neighborhood so that clearly from drawing 3 . Moreover, the rectifying characteristic which whose rectification ratio of **2V is 151 and was excellent was also accepted. Furthermore, the repeatability in nine components which consist of lap parts of a rectangular electrode was also good. Moreover, although the Scotch tape (trademark) was stretched on the vacuum deposition film of C60 and subsequently being removed, C60 vacuum-deposition film has arrived at the substrate firmly, and did not separate. Furthermore, although EPOSHIKI resin performed the protection coat on the front face of this component, it was almost changeless to tunnel current and a rectifying characteristic. Therefore, the component obtained by this example has the engine performance which was excellent as tunnel diode and a rectifying device, and having excelled also in repeatability and a mechanical strength was admitted.
[0028] (Example 1 of a comparison) In the example 1, the component was similarly formed except not performing heat-treatment for forming an aluminum oxide layer. And this was saved under the vacuum after component formation. The current-voltage characteristic in the dark was measured like the example 1 immediately after component formation. The result was shown as (b) among drawing 3 . Among drawing 3 , in (b), ** shows the forward current-voltage characteristic and ** shows the reverse current-voltage characteristic. The component obtained

here did not show the negative resistance and the rectifying action which are a tunnel diode property, but the rectification ratios of **1V were 1.2 and the value which was very inferior.
[0029] (Example 2) +2V were impressed to the aluminum electrode of the component produced like the example 1, and the homogeneous light of the wavelength of 400nm and optical on-the-strength 100 microwatt/cm 2 was irradiated. The big photocurrent of 1.3microA/cm2 was observed at this time, and it was admitted that the obtained component was excellent also as a photosensor. Furthermore, the photocurrent has been observed even if it changed wavelength in 400-800nm. Moreover, the repeatability in nine components which consist of lap parts of a rectangular electrode was also good.
[0030] (Example 2 of a comparison) The component was produced like the example 1 of a comparison. The 400nm same homogeneous light as an example 2 was irradiated at the aluminum electrode of the component immediately after production. Although the photocurrent of 0.1microA/cm2 was observed at this time, this value was a very small value as compared with the value observed in the example 2.
[0031] (Example 3) The tunnel diode which has the configuration shown in drawing 2 was produced. Up 0.5mmx3cm of the 2cmx3cm glass substrate 1 was covered, and on this substrate 1, vacuum deposition of the aluminum was carried out to the thickness of a 200 ONGUSU toe ROM, and it was referred to as electrode 2a (permeability of the 400nm homogeneous light; 2.18%). It once took out with this condition into air, and put in into the 80-degree C thermostat, annealing was performed under the air ambient atmosphere for 30 minutes, and the aluminum oxide layer 3 was formed on electrode 1a. The thickness of the aluminum oxide layer 3 was 100A in measurement of an ellipsomter. Furthermore, on this oxide layer 3, vacuum deposition of C60 was carried out to 1000A thickness like the example 1, and the vacuum deposition film 4 of C60 was formed. Subsequently, on it, vacuum deposition of 0.5cmx1.5cm copper-electrode 2b and the three pieces was carried out, and the component was formed. When the triangular wave which is -1V to +1V was impressed to this component from the function generator (scanning speed; 0.002Hz), the current-voltage characteristic showed the same tunnel diode property as (a) among drawing 3 . Moreover, repeatability was good about three electrodes.
[0032] (Example 3 of a comparison) 2000A of alpha-sesquithienyls was vapor-deposited like the example 3 on the top face of the glass plate 1 in which aluminum electrode 2a and the aluminum oxide layer 3 were formed (20A/(second)). If it is very hard to vapor-deposit alpha-sesquithienyl and it is vapor-deposited slowly, it will serve as film which decomposed and contained many impurities. Although decomposition will decrease if it vapor-deposits quickly (20A/(second) or more), an impurity is contained too. Subsequently, 0.5cmx1.5cm copper-electrode 2b and three pieces were formed by vacuum evaporationo. The triangular wave of -2 to +2V was impressed to the obtained component from the function generator (0.002Hz). This component showed a rectifying action, or did not show it, and its repeatability was very bad. Furthermore, negative resistance characteristic as tunnel diode was not observed at the time of the forward direction and reverse voltage impression.
[0033] (Example 4) The tunnel diode which has the configuration shown in drawing 2 was produced. On slide glass 1, indium electrode 2a was formed like the example 3. Then, the silicon oxide thin film 3 was formed by sputtering the whole surface on slide glass 1 and electrode 2a. Besides, it extracted from soot, vacuum deposition of this was carried out to the thickness of 1000A using fullerene mixing (containing C70 for C60 19% 80% in liquid chromatography analysis, remaining 1% was a 70 or more C high order fullerene compound) which removed insoluble matter with the chromatography, and the fullerene thin film 4 was formed. Subsequently, on it, vacuum deposition of 0.5cmx1.5cm silver electrode 2b and the three pieces was carried out, and the component was formed. When the current-voltage characteristic of the obtained component was measured like the example 3, when a minus electrical potential difference was impressed to an indium electrode, negative resistance was accepted, and it has checked that a tunnel diode property was shown.
[0034] (Example 5) In the configuration shown in drawing 2 , the tunnel diode which has the configuration which made reverse 1st electrode 2a and sequence of 2nd electrode 2b was produced. Width of face of 0.5cm and die length of 3cm were etched with the hydrochloric acid

on 3cm 2cmx ITO glass 1, the conductive film was removed (part equivalent to 1in drawing 2 a), and the conductive remaining film was made into indium oxide (ITO) electrode 2b. On this electrode 2b, the dispersion liquid (60; 20mg of C, vinyl acetate;20mg, ethyl acetate; dispersion liquid which put the glass bead into 200mg and were distributed with the paint shaker for 1 hour) which made vinyl acetate / ethyl-acetate solution distribute C60 were thin-film-ized using bar coating-machine #4, and the polymer distribution film 4 of C60 was produced. The vacuum drying of this film 4 was carried out at 100 degrees C for 1 hour. Thickness was 0.2 micrometers. Subsequently, by carrying out sputtering of the silicon in an oxygen ambient atmosphere on this film 4, the silicon oxide layer was made to form in the thickness of 80A, on it, vacuum deposition of the three aluminum (width-of-face [of 0.5cm], die length of 1.5cm) electrode 2a was carried out, and the component was constituted. The triangular wave of -2V to +2V was impressed at a scanning speed of 0.001Hz from the function generator between this indium oxide electrode 2b and aluminum electrode 2a. The current-voltage characteristic at this time showed negative resistance like (a) among drawing 3 at the time of reverse voltage impression, and also showed the rectifying action. Moreover, the repeatability in 3 sets of formed electrodes was good. Moreover, even if it carried out the protection coat of the whole with the epoxy resin, the current-voltage characteristic hardly changed. Therefore, the component obtained by this example has the engine performance which was excellent as tunnel diode and a rectifying device, and having excelled also in repeatability was admitted.
[0035] (Example 6) Tunnel diode was produced in the above-mentioned example 5, using the cast film as a fullerene thin film 4. Like the example 5, on indium oxide electrode 2b which etched indium tin glass 1 and was obtained, the liquid made to dissolve the carbon cluster C60 in toluene was dropped, and the cast film 4 of C60 was produced using the spinner. The vacuum drying was carried out at 100 more degrees C for 1 hour. Others formed the component similarly. When the electrical potential difference of 1V was impressed to this component and the homogeneous light of 400nm and 1 mW/cm2 was irradiated, the photocurrent of 1.5A was observed. Moreover, this component showed the good rectifying action and the tunnel diode property like the thing of an example 5.
[0036] (Example of reference) Commercial crude soot was refined and C60 and C70 were obtained. First, 4g (vacuum metallurgy incorporated company make) of crude soot containing fullerene was put into the extraction thimble, and it extracted by n-hexane;200ml for 24 hours using the Soxhlet extractor. Subsequently, the solvent was changed into mesitylene;200ml and the extract was performed for further 24 hours. When the first n-hexane solution was analyzed by liquid chromatography (silica gel - n-hexane), the ratio of C60:C70 is 9:1 and did not contain most of 76 or more C fullerene. The ratio of C60:C70 is about 6:4, and the mesitylene extract was carrying out variety content of the 76 or more C fullerene. n-hexane extract was condensed by the evaporator and 0.26g fullerene mixture was obtained. Using the ODS column, the mixed solvent of a 2-propanol / toluene;6/4 was used as the developing solution, and 0.21g and 0.02g of high grades C70 were obtained for the high grade C60 using inside low voltage preparative chromatograph. The mesitylene extract was condensed by the evaporator and mixed fullerene 0.13g was obtained. It isolated preparatively by the chromatograph similarly and mixture;0.01g of 60; 0.07g of high grades C, 70; 0.04g of high grades C, and other fullerene was obtained. Mixture contained C76, C78, C84, and fullerene with still larger molecular weight from GC-MS analysis.

[Translation done.]

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] It is what showed one example of the tunnel diode of this invention, and is the sectional view where (a) meets a top view and (b) meets the A-A line in (a).
[Drawing 2] It is what showed other examples of the tunnel diode of this invention, and is the sectional view where (a) meets a top view and (b) meets the A-A line in (a).
[Drawing 3] It is the graph which showed the current-voltage characteristic in an example and the example of a comparison.
[Description of Notations]
2a [-- Fullerene thin film] -- The 1st electrode, 2b -- The 2nd electrode, 3 -- An insulating layer, 4

[Translation done.]

* NOTICES *

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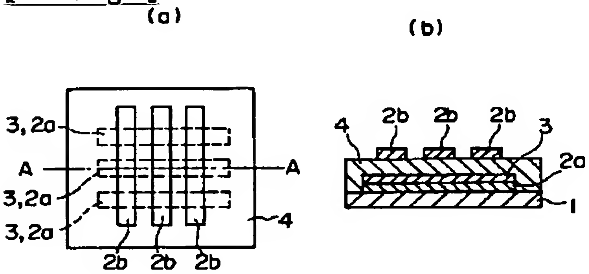
damages caused by the use of this translation.

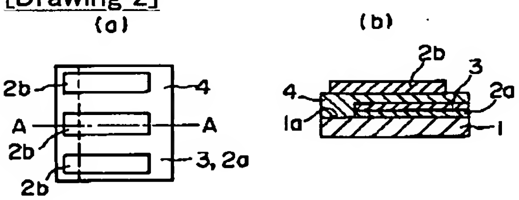
1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DRAWINGS

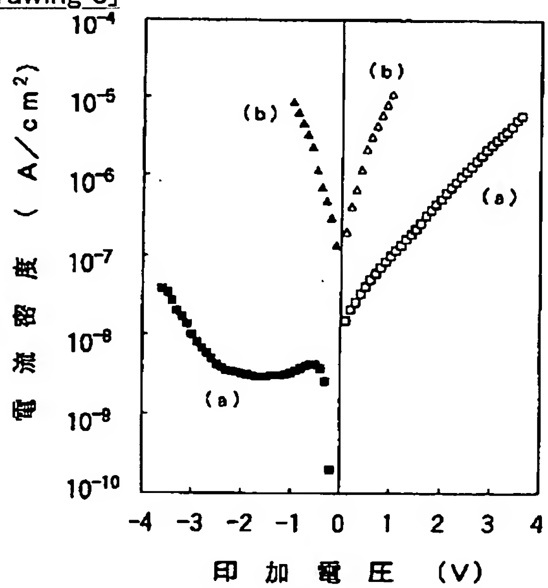
[Drawing 1]



[Drawing 2]



[Drawing 3]



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(54)【発明の名称】　トンネルダイオード

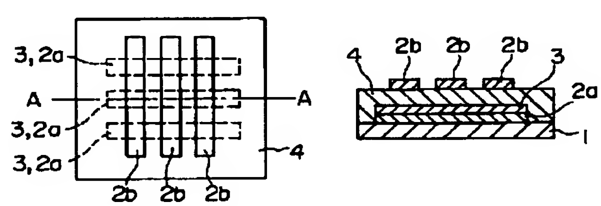
(57)【要約】

【目的】　有機物で構成される半導体素子であって、優れたトンネルダイオード特性を有する素子を提供する。

【構成】　フラーレン類、特にカーボンクラスターＣ６０および／またはＣ７０を好ましく用いて形成されるフラーレン薄膜４を、このフラーレン薄膜４に絶縁層３を介して接する仕事関数４．６未満の物質からなる第１の電極２ａと、フラーレン薄膜４に接する仕事関数４．６以上の物質からなる第２の電極２ｂとで挟持してトンネルダイオードを形成する。

【効果】　トンネルダイオード特性の他、良好な整流性、光センシング機能を有し、かつ機械的強度および再現性に優れた半導体素子が得られる。

(a)　(b)



【特許請求の範囲】

【請求項１】　フラーレン薄膜と、該フラーレン薄膜に接して設けられた絶縁層と、この絶縁層に接して設けられた仕事関数４．６未満の物質からなる第１の電極と、上記フラーレン薄膜に接して設けられた仕事関数４．６以上の物質からなる第２の電極とを有してなることを特徴とするトンネルダイオード。

【請求項２】　フラーレン薄膜が、カーボンクラスタで構成される薄膜であることを特徴とする請求項１記載のトンネルダイオード。

【請求項３】　フラーレン薄膜が、カーボンクラスタＣ６０および／またはカーボンクラスタＣ７０で構成される薄膜であることを特徴とする請求項２記載のトンネルダイオード。

【請求項４】　フラーレン薄膜が、真空蒸着膜、キャスト膜またはポリマー分散膜であることを特徴とする請求項１～３のいずれかに記載のトンネルダイオード。

【請求項５】　第１の電極および第２の電極が、金属または金属化合物からなる電極であることを特徴とする請求項１～４のいずれかに記載のトンネルダイオード。

【請求項６】　第１の電極がアルミニウムであり、かつ第２の電極が白金、金、銀、銅、酸化スズおよび酸化インジウムからなる群から選ばれる１種以上の材料からなる電極であることを特徴とする請求項５記載のトンネルダイオード。

【請求項７】　絶縁層が、アルミニウム酸化物層および／または珪素酸化物層であることを特徴とする請求項６記載のトンネルダイオード。

【請求項８】　絶縁層が、アルミニウム層を熱処理して生成された層であることを特徴とする請求項６記載のトンネルダイオード。

【請求項９】　絶縁層が、厚さ３０～１５０オングストロームの層であることを特徴とする請求項１～８のいずれかに記載のトンネルダイオード。

【請求項１０】　フラーレン薄膜が、第１の電極と第２の電極によりサンドイッチされていることを特徴とする請求項１～９のいずれかに記載のトンネルダイオード。

【請求項１１】　トンネルダイオードが、整流素子であることを特徴とする請求項１～１０のいずれかに記載のトンネルダイオード。

【請求項１２】　トンネルダイオードが、光センサーであることを特徴とする請求項１～１０のいずれかに記載のトンネルダイオード。

【発明の詳細な説明】

【０００１】

【産業上の利用分野】本発明は、有機半導体素子に係わり、特に優れた整流性および光導電性を有するトンネルダイオードに関する。

【０００２】

【従来の技術】半導体素子の分野では、従来、硫化カド

ミニウム、酸化亜鉛、結晶シリコン、アモルファスシリコン、ガリウム砒素などの無機物が使用されてきた。これらは、トランジスター、整流素子、ＩＣ、ＬＳＩ、光センサーおよび太陽電池等に使用されている。これらの半導体素子のなかでトンネル効果を奏するトンネルダイオードは、一般に、ＰＮ接合、あるいは金属（Ｍ）-絶縁層（Ｉ）-半導体（Ｓ）接合（ＭＩＳ接合）で構成され、ＰＮ接合の場合はＰ，Ｎともに高濃度にドーピングし、またＭＩＳ接合の場合は、絶縁層（Ｉ）の厚さを特定の範囲に規制して構成される。そして、①絶縁層が比較的厚い場合では、電流－電圧特性において、構成により順方向あるいは逆方向電圧印加時に電流極大を示し、その後、負性抵抗により電流値が減少し、また増加し始める特徴が得られ、②絶縁層が比較的薄い場合では、電流－電圧特性において、一定の電圧範囲において電流値が一定となる特徴が得られる（「Physics of Semiconductor Devices」、2nd　Edition、S.M.Sze,John Wiley & Sons,NY、513頁(1981年)）。このようなトンネルダイオードは、その特性により、高速スイッチング素子、マルチバイブレータ、高速論理回路、あるいは低雑音マイクロ波増幅器等に利用される。しかしながら、上記のような無機物を用いてこれらの半導体素子を作製するためには、高度な真空装置、高度な製膜技術および高度な純度規制等が要求され、その作製は容易にはなし得ないものであった。

【０００３】これに対して、有機物の多様性、半導体性等が注目されはじめ、ポリアセチレン、ポリピロール、フタロシアニン等の有機化合物の半導体性、導電性について多大な研究がなされてきた（「新・導電性高分子材料」、雀部博之監修、シーエムシー、（1987年））。そして、導電性高分子あるいは半導体性有機化合物を、金属で挟持してなる半導体素子として、ポリアセチレン、ポリジアセチレン、ポリピロール、α－セスキチエニル、フタロシアニン等の半導体薄膜（Ｓ）を金属電極（Ｍ）で挟持してなるＭＳ素子、あるいはそれらの間に絶縁体の薄膜（Ｉ）を挟持してなるＭＩＳ素子等、多くの素子が提案されている（「Physics of Semiconductor Devices」、2nd　Edition、S.M.Sze,John Wiley & Sons,NY(1981年)、D.Fichou,F.Garnieret al., CHEMTRONICS, 1988年,176頁）。

【０００４】これらの有機化合物はＰ型あるいはＮ型の半導体性を示し、これを、その有機化合物のフェルミ準位と比較して、仕事関数の小さい電極と仕事関数の大きい電極とで挟持したときに整流性を示すものである。例えば、α－セスキチエニルの場合（D.Fichou,F.Garnier et al., CHEMTRONICS, 1988年,176頁）、これをアルミニウム電極とインジウムスズオキサイド（あるいは金）電極とで挟持したとき、±１Ｖで１００倍以上の整流性を示す。さらに、異種導電性高分子の接合で、整流素子を構築した例（Pt｜ﾎﾟﾘﾋﾟﾛｰﾙ｜ﾎﾟﾘﾁｵﾌｪﾝ｜In、M.Aizaw

a,H.Shirakawa,Synth.Met., 18号, 711頁(1987年)）や、ＦＥＴ を構築した例（H.Koezuka, etal., Synth.Met., 18号, 699頁(1987年)）も知られている。また、フタロシアニン等は光導電性を示すことから、太陽電池等への応用が検討され、これをアルミニウムおよびＩＴＯガラス（酸化インジウムでヘビードープした酸化スズ薄膜による導電性ガラス）で挟持してなる太陽電池が検討されている。しかしながら、有機化合物を用いたトンネルダイオードに関する報告は見あたらないのが現状である。

【０００５】

【本発明が解決しようとする課題】上記の有機化合物は一般に、①Ｓ層すなわち導電性高分子層あるいは有機半導体層の不安定性（例えばポリアセチレンの空気や湿度等に対する不安定性、ドーピング後の不安定性等）、②不純物の混入による再現性の低下（例えばα－セスキチエニル、フタロシアニン等は濃硫酸程度しか溶解する溶媒がなく、純度の向上が非常に困難である）、③素子形成時の不確定性（気相重合、電解重合等による触媒、電解質等の混入等、α－セスキチエニル、フタロシアニン等の真空蒸着時の熱分解による不純物の混入等）、④素子形成後の電極の腐食（ドーパントによる電極の腐食、フタロシアニンに見られるようなアルミニウム電極の酸化促進等）、⑤薄膜の機械的脆さ（α－セスキチエニル、フタロシアニン等の真空蒸着膜はこすると剥がれる）等の問題を有するものであり、いずれも実用化に至っていない。さらに太陽電池では、その経時劣化、変換効率の低さから実用化に至っていない。わずかに有機物で実用化されたものは、ポリアニリンを用いたポリマーバッテリー、ＴＣＮＱを用いたコンデンサー、フタロシアニン等を用いた電子写真感光体程度であり、見るべき成果がないのが現状である。

【０００６】

【課題を解決するための手段】本発明者らは、従来の導電性高分子をはじめとする有機半導体の上記の如き種々の欠点に鑑み、これらを改良すべく鋭意検討を行った結果、フラーレン薄膜を用い、これに接するように２つ以上の電極を設けることにより、容易に再現性よく半導体素子が得られること、そして、特定の電極を用い、電極とフラーレン層の間に絶縁層を設けることでトンネルダイオード特性が得られることを見いだし、本発明を完成するに至った。

【０００７】すなわち、前記課題を解決するために、本発明のトンネルダイオードは、フラーレン薄膜と、該フラーレン薄膜に接して設けられた絶縁層と、この絶縁層に接して設けられた仕事関数４．６未満の物質からなる第１の電極と、上記フラーレン薄膜に接して設けられた仕事関数４．６以上の物質からなる第２の電極とを有するものである。

【０００８】以下、本発明を詳しく説明する。本発明は、フラーレン薄膜（Ｓ）と、これに接する絶縁層（Ｉ）と、絶縁層に接する第１の電極（Ｍ）と、フラーレン薄膜に接する第２の電極とを有するＭＩＳトンネルダイオードを提供するものである。図１は本発明のトンネルダイオードの一実施例を示したもので、（ａ）は平面図、（ｂ）は（ａ）中のＡ－Ａ線に沿う断面図である。図１に示したトンネルダイオードは、絶縁基板１上に、短冊状に形成された３つの第１の電極２ａ，２ａ，２ａが平行に設けられ、これら第１の電極２ａ，２ａ，２ａの上面に絶縁層３が形成され、絶縁層３および絶縁基板１の上面にフラーレン薄膜４が形成され、さらにこのフラーレン薄膜４上に短冊状に形成された３つの第２の電極２ｂ，２ｂ，２ｂが平行に、かつ上記第１の電極２ａ，２ａ，２ａと直交するように設けられている。ここで絶縁層３は、第１の電極２ａ上だけでなく、第１の電極２ａおよび基板１上の全面に形成してもよい。さらに必要に応じて、第２の電極２ｂ，２ｂ，２ｂおよびフラーレン薄膜４上に絶縁性ポリマー膜あるいは絶縁性金属酸化物等の保護膜を形成することもできる。また、第１の電極および第２の電極の数は、それぞれ１以上に任意に設定することができる。

【０００９】本発明で用いられるフラーレン薄膜４は、フラーレン類を用いて形成された薄膜である。ここで、フラーレン類とは、ｓｐ２炭素よりなる球状あるいはラグビーボール状のカーボンクラスタの総称であり、一般にＣ６０、Ｃ７０、Ｃ７６、Ｃ７８、Ｃ８２、Ｃ８４、Ｃ９０、Ｃ９６等が知られている。これらは、炭素をアーク放電あるいは抵抗加熱して気化させ、ヘリウム等の不活性ガスで急冷して生成したすすの中等に含有され（例えば、Kraetschmer等、Nature､347号、354頁(1990年)等）、Ｃ６０が最も多く含有されている。そしてこのすすから、例えばヘキサン、ベンゼン、トルエン、メシチレン、二硫化炭素等の溶媒で抽出することによって上記カーボンクラスタの混合物が得られる。さらにこの混合物を精製し、各々単離するには、通常有機化合物の精製に用られるクロマトグラフィーの手法（例えば、Kraetschmer等、Nature､347号、354頁(1990年)等）を用いることができる。本発明においては、合成、単離が容易なＣ６０またはＣ７０、あるいはこれらを含有するすすから抽出、不溶性不純物除去を施して得られる混合フラーレンが好ましく用いられる。

【００１０】フラーレン薄膜４は各種の製膜方法により形成して用いることができ、例えば真空蒸着膜、キャスト膜およびポリマー分散膜等を用いることができる。真空蒸着膜は、例えば一般的真空蒸着の手法に従い（薄膜ハンドブック、日本学術振興会薄膜第１３１委員会編、オーム社（1984年） 等）、５×１０$^{-5}$ ｔｏｒｒ以下の真空下で、金属性ボートあるいはアルミナ性ボートなどを用いてフラーレン類を加熱し、その上部あるいは下部に基板を置くことで薄膜を形成できる。この際、必要に

応じ、基板を加熱あるいは冷却しても良い。基板を冷却した場合、薄膜はアモルファス状態となり、また、室温あるいはそれ以上に加熱した場合は結晶状態として得られる。このフラーレン類の真空蒸着膜は空気中で安定で、かつ非常に硬く強固である。例えば、従来のフタロシアニン、α－セスキチエニル等はこすれば剥がれ、セロテープ等により簡単に剥離できるように機械的強度に劣るのに対し、フラーレン類の蒸着膜はこすってもなかなか剥がれず、セロテープでは剥離できない強固な膜であり、機械的強度に優れる。

【００１１】キャスト膜は、例えばフラーレン類がベンゼン、トルエン、メシチレン等芳香族炭化水素、二硫化炭素、ｎ－ヘキサン等に溶解する性質を利用するもので、簡便に薄膜を作成しうる手段である。すなわち上記溶媒等に溶解せしめ、基板上に滴下する、あるいは基板をスピンナー上に固定し、上記溶解液を滴下した後、スピンナーを適当な回転数で回転せしめ薄膜化する、あるいは基板上に滴下した溶液をバーコーターまたはドクターブレード等を用いて薄膜化するなどの手段で薄膜化し、次いで自然乾燥、あるいは熱または真空乾燥するなどの手段で乾燥することによって製膜することができる。

【００１２】ポリマー分散膜は、例えばポリマーの溶液中にフラーレン類を添加し、溶解あるいは分散せしめた後、上記キャスト膜と同様の手段で製膜することができる。分散方法としては、ペイントシェーカー、スペックスミキサーミル、サンドミル、ボールミル、アトラター、ニーダー等の顔料分散手法を用いることができる。ここで用いることができるポリマーとしては、特に制限はないが、例を挙げると、飽和ポリエステル、不飽和ポリエステル、ポリカーボネート、ポリ塩化ビニール、ポリ酢酸ビニール、ポリビニールカルバゾール、スチレン等のビニール系ポリマー、フッ化ポリビニリデン、フッ化ポリビニル等のフッ素化ポリマー、スチレン－マレイン酸等のコポリマー等がある。また、例えば、ポリアクリレート系液晶高分子、ポリシロキサン系液晶高分子等の液晶高分子を用いることもできる。

【００１３】トンネルダイオードを構成するフラーレン薄膜４の膜厚については、薄すぎるとお互いの電極が短絡し易いので、ある程度の厚さのあるものが好ましい。したがって、フラーレン薄膜４の膜厚は１００オングストローム～１００μｍの範囲が好適であり、特に好ましくは、２００オングストローム～１０μｍの範囲である。

【００１４】フラーレンの優れた半導体性を引き出すには、少なくともフラーレン薄膜４に絶縁層３を介して接する第１の電極２ａと、フラーレン薄膜４に接する第２の電極２ｂを設けることが必要である。これらの電極としては、例えば金属電極、金属酸化物電極、および炭素電極等を用いることができる。第１の電極２ａとしては、CRC Habdbook of Chemistry and Physics, CRC Press, 12-97(1991年)に記載された仕事関数であって、４．６未満の仕事関数を有する物質を用いることができ、例示するならばリチウム、ナトリウム、マグネシウム、アルミニウム、カリウム、インジウム、カルシウム、亜鉛、スカンジウム、チタン、マンガン、ジルコニウム、ガリウム、ニオブ、アンチモン、およびサマリウム等の金属を用いることができ、特にアルミニウムが好ましく用いられる。

【００１５】また、第２の電極２ｂとしては４．６以上の仕事関数を有する物質を用いることができ、例えば、パラジウム、テルル、レニウム、イリジウム、銅、銀、金、白金、ルテニウム、ゲルマニウム、酸化スズ（例えばＮＥＳＡガラス）、酸化インジウム、酸化インジウムでヘビードープした酸化スズ（例えばＩＴＯガラス）、酸化亜鉛、グラファイト、グラッシーカーボン、銀ペーストおよびカーボンペースト等の金属あるいは金属酸化物等が用いられるが、特に、白金、金、銀、銅、酸化スズ（例えばＮＥＳＡガラス、ＮＥＳＡコートポリマー膜）および酸化インジウム（例えばＩＴＯガラス、ＩＴＯコートポリマー膜）が好ましい。

【００１６】これらの電極は、例えば金属板、炭素板、薄膜、導電性塗料膜等いずれの形態でも使用する事ができる。薄膜の形態で使用するとき、金属箔、蒸着膜、スパッタリング膜、電着膜、スプレー熱分解膜等の手段で薄膜化して使用することができる。また、導電性塗料（例えば銀、炭素含有塗料）を塗布して電極を形成することもできる。ここで、製膜あるいは塗布によって電極を設ける場合には、基板１を用いることが好ましい。この基板１としては特に制限はなく、絶縁性のものが好ましい。その例としては、ガラス板、石英板、絶縁性ポリマー板等が挙げられる。また、電極として金属板、炭素板等、板状の電極を用いるときは、特に基板１を用いなくても良い。

【００１７】本発明のトンネルダイオードにおいて、そのトンネル効果を得るためには仕事関数の小さい第１の電極２ａとフラーレン薄膜４の間に薄い絶縁層３を有することが必須条件である。この絶縁層３としては、金属酸化物、有機化合物、ポリマー絶縁層等を用いることができる。金属酸化物層としては、アルミニウム酸化物、酸化珪素、酸化インジウム、酸化スズ、および酸化チタン等が挙げられる。有機化合物あるいはポリマー絶縁層としては、通常の絶縁性有機化合物あるいはポリマーであれば良く、例示するならば、脂肪酸、長鎖アルコール、ポリエチレン、ポリ塩化ビニル、ポリアクリロニトリル、エポキシ樹脂、およびポリアミド等が挙げられる。尚、本発明はここに例示の化合物に限定されるものではない。

【００１８】これら絶縁層３は、蒸着、スパッタリング、キャスティング、ＬＢ膜等の手法により容易に形成

することができる。また、絶縁層３として、アルミニウム酸化物、酸化珪素はその形成が容易なことから特に好ましい。アルミニウム酸化物絶縁層の場合、蒸着により得たアルミニウム層を空気等の酸素含有気体中で熱処理することで、これを容易に形成することができる。酸化珪素絶縁層は、シリコンを酸素雰囲気下でスパッタリングすること、あるいは珪素の蒸着膜を空気等の酸素含有気体中で熱処理することで、これを容易に形成することができる。これらの絶縁層形成工程において、熱処理温度は特に制限されないが、５０～１０００℃の温度が作業性の点からも好ましい。特に、アルミニウム層を酸化する場合は５０～２００℃の温度が好適であり、珪素層を酸化する場合は２００～８００℃の温度が好適である。またトンネルダイオードの構成において、絶縁層３の厚さは特に重要であり、１０～２００オングストローム、特に３０～１５０オングストロームの厚さが好ましい。

【００１９】本発明のトンネルダイオードは、例えば以下のようにして作製することができる。まず基板１を用意する。次に、その基板１上に第１の電極２ａを蒸着あるいはスパッタリング等の手段により形成する。そして、この第１の電極２ａが酸化され易い金属電極の場合には、空気等の酸素含有気体中で熱処理を施して酸化物絶縁層３を形成する。さらにその絶縁層３上に、蒸着、キャスティングあるいはポリマー分散膜等の手段でフラーレン薄膜４を形成する。次いで、フラーレン薄膜４上に、第２の電極２ｂを蒸着、スパッタリング等の手段で形成することでトンネルダイオードを作製することができる。あるいは、絶縁性基板１上にまず第２の金属電極を形成した後に、フラーレン薄膜４、絶縁層３、第１の電極２ａを順次製膜してトンネルダイオードを作製することもできる。

【００２０】本発明のトンネルダイオードにあっては、暗中での電流－電圧特性測定において、０Ｖから逆方向に電圧を掃引したとき、電流の極大値を示した後、次いで負性抵抗を示すためその電流値が減少し、その後、電流値の増加が認められ、トンネルダイオードとしての特徴ある性質が得られる。

【００２１】また、本発明のトンネルダイオードは、優れたトンネルダイオード特性を示すとともに、優れた整流性、および光導電特性を示し、トンネルダイオードとしての用途、すなわち高速スイッチング素子、マルチバイブレータ、高速論理回路、低雑音マイクロ波増幅器等のみならず、整流素子、光スイッチ、光センサーにも用いることができる。

【００２２】尚、本発明のトンネルダイオードは、上記の例の構成に限定されるものではなく、種々の形態が可能であり、結晶、粉末等で構成されても良い。また、トンネルダイオードの使用目的により種々の形態をとることができ、これらの目的に基づき、電極および素子の構成は適宜変更されうるものである。

【００２３】ここで、トンネルダイオードおよび整流素子として使用するとき、電極の膜厚は任意とすることができる。これに対して光センサーとして使用するときは、光を入射する側の電極は半透明である必要がある。酸化物電極を用いるときは、光の透過率が９８％～０．１％の範囲が用いられるが、光の透過率が大きい方が光に対する応答性は高い。金属電極の場合、光の透過率が大きい方が光に対する応答性は高いが、透過率が大きすぎると電極が電流を通さない。従って、光の透過率は５０％～０．１％の範囲が好適に用いられる。

【００２４】電極の構成を、図１に示したようなサンドイッチ電極としたものは、集積化した整流素子（例えばスイッチング素子等）に好適に用いることができ、例えば、液晶、ＥＣＤ等の駆動を行うことができる。または、光センサー（例えばイメージセンサー等）としても好適に用いることができる。これらの場合、外部駆動装置（図示せず）から互いに直行する第１の電極２ａおよび第２の電極２ｂに電場を印加して、整流素子あるいは光センサーとして用いることができる。

【００２５】図２はサンドイッチ電極を用いた本発明のトンネルダイオードの他の例を示したもので、（ａ）は平面図、（ｂ）は（ａ）中のＡ－Ａ線に沿う断面図である。このものは絶縁基板１上に、第１の電極２ａが設けられ、この第１の電極２ａ上（あるいは第１の電極２ａおよび絶縁基板１上全面）に絶縁層３が設けられ、その上部全面にフラーレン薄膜４が形成され、さらにフラーレン薄膜４上には、短冊状に形成された第２の電極２ｂが設けられている。この第２の電極２ｂの数は、１以上の任意の数に設定することできる。尚、第２の電極２ｂは、短冊状だけでなく、円、楕円等いかなる形状でもよい。また、第１の電極２ａは、基板１上面の一方の端縁部１ａを残して太い帯状に形成され、第２の電極２ｂは、先に形成した第１の電極２ａの長手方向に直交し、かつこの第１の電極２ａ上から上記絶縁基板１の端縁部１ａ上に渡って位置するように設けられ、このことにより第１の電極および第２の電極からの配線が短絡する不都合を防止することができる。また必要に応じ、第２の電極２ｂおよびフラーレン薄膜４上に絶縁性ポリマー膜あるいは絶縁性金属酸化物等の保護膜を形成することもできる。このように構成されたトンネルダイオードは、単独の整流素子、トランジスター、光センサー等にも有効に用いることができる。

【００２６】

【実施例】（実施例１）図１に示した構成を有するトンネルダイオードを作製した。スライドガラス１上に、幅３ｍｍ、長さ２０ｍｍの形状の第１の電極２ａを３ｍｍの間隔で３個、真空蒸着により形成した。この電極２ａにはアルミニウムを使用し、5×10^{-5} ｔｏｒｒの真空下で２００オングストロームの厚さに形成した。この電極２ａ、３個を形成したスライドガラス１を真空蒸着器

のアルミナルツボ上２０ｃｍに置き、カーボンクラスタＣ６０をアルミナ製ルツボに入れ、5×10^{-6} ｔｏｒｒの真空下で５２０～５５０℃に加熱しながら蒸着させ（５オングストローム／秒）、Ｃ６０の真空蒸着膜４を１０００オングストロームの厚さに形成した。次いで、金電極２ｂ、３個を２００オングストロームの厚さに形成して素子を作製した。この素子を１００℃に加熱したオーブン中に入れ、空気雰囲気下で２０分加熱処理した。このとき、アルミニウム電極２ａとＣ６０薄膜４の間にアルミニウム酸化物層３が、エリプソメーターでの測定によると６０オングストロームの厚さに形成されていた。

【００２７】このようにして得られた素子を暗中に保持し、第１の電極（アルミニウム）２ａに、±３．６Ｖの三角波をファンクションジェネレータを用いて０．００１Ｈｚの掃引速度で印加した。この時、流れる電流をエレクトロメータを用いて測定した。測定により得られた電流－電圧特性を、片対数図として図３中（ａ）で示した。図３中（ａ）において、□は順方向電流－電圧特性を示し、■は逆方向電流－電圧特性を示す。尚、図３においてマイナス電圧印加時の電流の実測値はマイナスで有るが、ここでは電流の絶対値で示した。図３から明らかなように、逆方向電圧印加時において、まず－０．５Ｖ付近に極大値を示し、ついでトンネルダイオード特性である負性抵抗によって電流値は減少し、－２Ｖ付近から電流値が増加することが認められた。また、±２Ｖの整流比は１５１であり優れた整流特性も認められた。さらに、直交電極の重なり部分で構成される９個の素子における再現性も良好であった。また、Ｃ６０の真空蒸着膜上にセロテープをはり、ついで剥がしたが、Ｃ６０真空蒸着膜は強固に基板に着いており、剥がれなかった。さらに、この素子の表面にエポシキ樹脂で保護コートを行ったが、トンネル電流および整流特性にほとんど変化はなかった。したがって、本実施例で得られた素子は、トンネルダイオードおよび整流素子として優れた性能を有しており、再現性、機械的強度にも優れていることが認められた。

【００２８】（比較例１）実施例１において、アルミニウム酸化物層を形成するための加熱処理を行わない以外は同様にして素子を形成した。そして素子形成後、これを真空下に保存した。素子形成直後、実施例１と同様に暗中の電流－電圧特性を測定した。その結果を図３中（ｂ）として示した。図３中（ｂ）において、△は順方向電流－電圧特性を示し、▲は逆方向電流－電圧特性を示す。ここで得られた素子は、トンネルダイオード特性である負性抵抗および整流性を示さず、±１Ｖの整流比は１．２と非常に劣った値であった。

【００２９】（実施例２）実施例１と同様に作製した素子のアルミニウム電極に＋２Ｖを印加し、波長４００ｎｍ、光強度１００μＷ／cm^2の単色光を照射した。この時１．３μＡ／cm^2の大きな光電流が観測され、得られた素子が光センサーとしても優れていることが認められた。さらに、光電流は波長を４００～８００ｎｍの範囲で変化させても観測できた。また、直交電極の重なり部分で構成される９個の素子における再現性も良好であった。

【００３０】（比較例２）比較例１と同様にして素子を作製した。作製直後の素子のアルミニウム電極に、実施例２と同様の４００ｎｍの単色光を照射した。この時、０．１μＡ／cm^2の光電流が観測されたが、この値は実施例２で観測された値に比して、非常に小さい値であった。

【００３１】（実施例３）図２に示した構成を有するトンネルダイオードを作製した。２ｃｍ×３ｃｍのガラス基板１の上部０．５ｍｍ×３ｃｍを遮蔽し、この基板１上にアルミニウムを２００オングストーロムの厚さに真空蒸着して電極２ａとした（４００ｎｍの単色光の透過率；２．１８％）。この状態で一旦空気中に出し、８０℃の恒温槽中に入れ、空気雰囲気下で３０分アニーリングを行い、電極１ａ上にアルミニウム酸化物層３を形成した。アルミニウム酸化物層３の膜厚はエリプソメーターの測定で１００オングストロームであった。さらにこの酸化物層３上に実施例１と同様にしてＣ６０を１０００オングストロームの膜厚に真空蒸着し、Ｃ６０の真空蒸着膜４を形成した。ついで、その上に０．５ｃｍ×１．５ｃｍの銅電極２ｂ、３個を真空蒸着し、素子を形成した。この素子に－１Ｖから＋１Ｖの三角波をファンクションジェネレータから印加した（スキャンスピード；０．００２Ｈｚ）ところ、電流－電圧特性は図３中（ａ）と同様なトンネルダイオード特性を示した。また、３個の電極について再現性は良好であった。

【００３２】（比較例３）実施例３と同様にして、アルミニウム電極２ａおよびアルミニウム酸化物層３を形成したガラス板１の上面に、α－セスキチエニルを２０００オングストローム蒸着した（２０オングストローム／秒）。α－セスキチエニルは、非常に蒸着しづらく、ゆっくり蒸着すると、分解し不純物を多く含んだ膜となる。速く（２０オングストローム／秒以上）蒸着すれば分解は少なくなるが、やはり不純物を含有する。次いで、０．５ｃｍ×１．５ｃｍの銅電極２ｂ、３個を蒸着により形成した。得られた素子に、－２から＋２Ｖの三角波をファンクションジェネレータから印加した（０．００２Ｈｚ）。この素子は、整流性を示したり、示さなかったりし、再現性が非常に悪かった。さらに順方向、逆方向電圧印加時にトンネルダイオードとして特徴的な負性抵抗は観測されなかった。

【００３３】（実施例４）図２に示した構成を有するトンネルダイオードを作製した。スライドガラス１上に、実施例３と同様にして、インジウム電極２ａを形成した。引き続き、スライドガラス１上および電極２ａ上の

全面に、珪素酸化物薄膜３をスパッタリングにより形成した。この上に、すすから抽出し、クロマトグラフィーで不溶物を除去したフラーレン混合（液体クロマトグラフィー分析ではＣ６０を８０％、Ｃ７０を１９％含有し、残り１％はＣ７０以上の高次のフラーレン化合物であった）を用いて、これを１０００オングストロームの厚さに真空蒸着し、フラーレン薄膜４を形成した。次いで、その上に０．５ｃｍ×１．５ｃｍの銀電極２ｂ、３個を真空蒸着して、素子を形成した。得られた素子の電流－電圧特性を実施例３と同様にして測定したところ、インジウム電極にマイナス電圧を印加した時に負性抵抗が認められ、トンネルダイオード特性を示すことが確認できた。

【００３４】（実施例５）図２に示した構成において、第１の電極２ａと第２の電極２ｂの順序を逆にした構成を有するトンネルダイオードを作製した。２ｃｍ×３ｃｍのＩＴＯガラス１上において、幅０．５ｃｍ、長さ３ｃｍを塩酸でエッチングして導電性膜を除去（図２中１ａに相当する部分）し、残りの導電性膜を酸化インジウム（ＩＴＯ）電極２ｂとした。この電極２ｂ上に、Ｃ６０を酢酸ビニル／酢酸エチル溶液に分散させた分散液（Ｃ６０；２０ｍｇ、酢酸ビニル；２０ｍｇ、酢酸エチル；２００ｍｇにガラスビーズを入れペイントシェーカーで１時間分散した分散液）をバーコーター＃４を用いて薄膜化し、Ｃ６０のポリマー分散膜４を製膜した。この膜４を１００℃で１時間、真空乾燥した。膜厚は、０．２μｍであった。ついで、この膜４上に珪素を酸素雰囲気でスパッタリングすることにより珪素酸化物層を８０オングストロームの厚さに形成させ、その上にアルミニウム（幅０．５ｃｍ，長さ１．５ｃｍ）電極２ａを３個、真空蒸着して素子を構成した。この酸化インジウム電極２ｂとアルミニウム電極２ａの間に－２Ｖから＋２Ｖの三角波を、ファンクションジェネレータより、０．００１Ｈｚのスキャンスピードで印加した。この時の電流－電圧特性は、図３中（ａ）と同様に逆方向電圧印加時に負性抵抗を示し、整流性も示した。また、形成された３組の電極における再現性は良好であった。また、エポキシ樹脂で、全体を保護コートしても電流－電圧特性はほとんど変化しなかった。従って、本実施例で得られた素子は、トンネルダイオードおよび整流素子として優れた性能を有し、再現性にも優れたものであることが認められた。

【００３５】（実施例６）上記実施例５において、フラーレン薄膜４としてキャスト膜を用いてトンネルダイオードを作製した。実施例５と同様にして、インジウムスズガラス１をエッチングして得られた酸化インジウム電極２ｂ上に、カーボンクラスタＣ６０をトルエンに溶解させた液を滴下し、スピンナーを用いて、Ｃ６０のキャスト膜４を製膜した。さらに１００℃で、１時間、真空乾燥した。他は同様にして素子を形成した。この素子に１Ｖの電圧を印加し、４００ｎｍ、１ｍＷ／ｃｍ^{2}の単色光を照射したところ、１．５Ａの光電流が観測された。また、この素子は実施例５のものと同様に良好な整流性およびトンネルダイオード特性を示した。

【００３６】（参考例）市販の粗製すすを精製してＣ６０およびＣ７０を得た。まず、フラーレン類を含有する粗製すす（真空冶金株式会社製）４ｇを円筒濾紙に入れ、ソックスレー抽出器を用い、ｎ－ヘキサン；２００ｍｌで２４時間抽出した。ついで、溶媒をメシチレン；２００ｍｌに変更し、さらに２４時間抽出を行った。初めのｎ－ヘキサン溶液を液体クロマトグラフィ（シリカゲル～ｎ－ヘキサン）で分析したところ、Ｃ６０：Ｃ７０の比は９：１であり、Ｃ７６以上のフラーレンをほとんど含有していなかった。メシチレン抽出液は、Ｃ６０：Ｃ７０の比は約６：４であり、Ｃ７６以上のフラーレンを多種含有していた。ｎ－ヘキサン抽出液をエバポレータで濃縮し、０．２６ｇのフラーレン混合物を得た。ＯＤＳカラムを用い、２－プロパノール／トルエン；６／４の混合溶媒を展開液とし、中低圧分取クロマトグラフを用いて、高純度Ｃ６０を０．２１ｇ、高純度Ｃ７０を０．０２ｇ得た。メシチレン抽出液をエバポレータで濃縮し、混合フラーレン０．１３ｇを得た。同様にクロマトグラフで分取して、高純度Ｃ６０；０．０７ｇ、高純度Ｃ７０；０．０４ｇ、その他フラーレン類の混合物；０．０１ｇを得た。混合物は、ＧＣ－ＭＳ分析からＣ７６、Ｃ７８、Ｃ８４およびさらに分子量の大きいフラーレン類を含有していた。

【００３７】

【発明の効果】以上説明したように、本発明のトンネルダイオードは、フラーレン薄膜と、該フラーレン薄膜に接して設けられた絶縁層と、この絶縁層に接して設けられた仕事関数４．６未満の物質からなる第１の電極と、上記フラーレン薄膜に接して設けられた仕事関数４．６以上の物質からなる第２の電極とを有してなるものである。本発明のトンネルダイオードは、優れたトンネルダイオード特性を示すとともに、優れた整流性、光導電性を示し、これを好適に用いて各種の半導体素子を構成することができる。そして、本発明で用いられるフラーレン類は、合成が容易で、かつ溶媒に溶解するため、精製が容易で高純度品を容易に得ることができる。また、耐熱性も高く、蒸着時の分解も起こらないため、容易に素子化を行うことができる。したがって、再現性の良いトンネルダイオードが得られる。また、本フラーレン類は、真空を必要としないキャスト膜、ポリマー分散膜の形でも使用できる。したがって、本発明のトンネルダイオードは、フラーレン類を製膜して得られるフラーレン薄膜を用いることにより、良好な安定性、再現性が得られる。さらに、本発明のトンネルダイオードは樹脂等を用いた保護コートを施してもその性能が変化しない為、広範な用途に用いることができる。特に、整流素子、整

流性を用いた液晶、ＥＣＤ素子等の駆動素子、光センサー、あるいは光センサー機能を応用したイメージセンサー等に幅広く応用することができる。

【図面の簡単な説明】

【図１】　本発明のトンネルダイオードの一実施例を示したもので、（ａ）は平面図、（ｂ）は（ａ）中のＡ－Ａ線に沿う断面図である。

【図２】　本発明のトンネルダイオードの他の実施例を

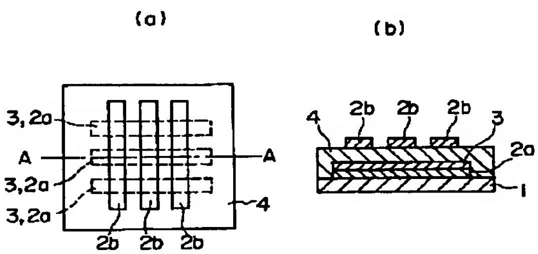
示したもので、（ａ）は平面図、（ｂ）は（ａ）中のＡ－Ａ線に沿う断面図である。

【図３】　実施例および比較例における電流－電圧特性を示したグラフである。

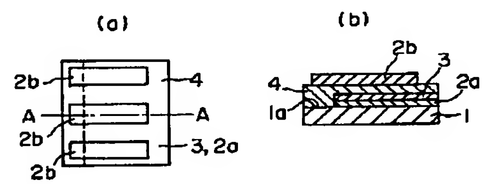
【符号の説明】

２ａ…第１の電極、２ｂ…第２の電極、３…絶縁層、４…フラーレン薄膜

【図１】



【図２】



【図３】